DERICK

Molecular rearrangements & the constitution of Laurolene

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MOLECULAR REARRANGEMENTS AND THE CONSTITUTION OF LAUROLENE

BY

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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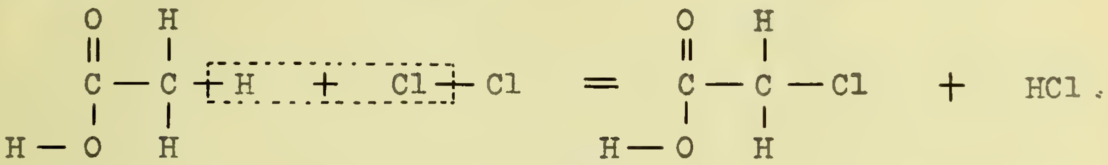
MOLECULAR
REARRANGEMENTS AND THE
CONSTITUTION OF
LAUROLENE

PART I.

MOLECULAR REARRANGEMENTS.

INTRODUCTION.

In recent years the study of the mechanism of reactions of organic chemistry has received the major part of the organic chemist's interest. One of the most difficult and, therefore, last problems to be attacked is that phenomenon known as substitution. Until very recently no explanation of substitution has been attempted. To show the substitution of one methane hydrogen atom of acetic acid by chlorine, the following graphical scheme has been much used:



$$\begin{array}{ccccccccccccc} & O & & H & & & & & O & & H & & \\ & \| & & | & & & & & \| & & | & & \\ & C & - & C & -\boxed{H \quad + \quad Cl}- & Cl & = & & C & - & C & -Cl & + \quad HCl. \\ & | & & | & & & & & | & & | & & \\ H- & O & & H & & & & H- & O & & H & & \end{array}$$

From this graphical method of writing the reaction it is evident that the substituting chlorine atom is assumed to replace the hydrogen atom which has formed hydrochloric acid with the remaining atom of the chlorine molecule. That is, the chlorine atom is held to the methane carbon with the same valence that originally held the hydrogen atom. The only explanation offered as a reason that chlorine should replace the hydrogen being that there is a much greater tendency for chlorine to unite with hydrogen than with itself or carbon. It is very evident that this is little better than no explanation at all for under very slightly different conditions the chlorine may be replaced by hydrogen. Such then, has been the state of affairs with one of the most important phenomena of organic chemistry.

In recent years, A. Michael [1] of Tufts College, has been studying this phenomenon in the light of his many years of very successful work in this branch of science. He concludes that all

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[1] See Henrich, "Neuere Theoretische Anschauungen auf dem Gebiete der organischen Chemie". p. 239.

so called substitution reactions are preceeded by intermediate additive reactions, thereby following a suggestion made by Kekule[1]over fifty years ago and later emphasized by Van't Hoff [2]. This explanation of substitution may be represented graphically by using the illustration given by Kekule. Given the two diatomic molecules ●● and ○○ which react by substitution to form two new molecules, ●○ and ●○ , then Kekule said the following occurred.

Michael to explain this, states that all of the combining energy of any atom is never completely used up when it unites to form molecules. Hence molecules also possess a certain amount of combining energy which varies according to the strength of the union between the atoms in the original molecule. By virtue of this free combining energy, molecules unite with each other to form compounds, which must be very unstable when compared with the original molecules. This intermediate unstable compound will suffer a rearrangement of all of the atoms concerned, provided a new compound or compounds may result which will show an increase in entropy. Briefly stated, the above is Michael's explanation of the phenomenon of substitution.

Nef, [3] at Chicago University, has been giving this phenomenon the benefit of his many years of very successful work in the field of organic chemistry. His views are the result of his work upon the divalent carbon atom and are very similar to those held by

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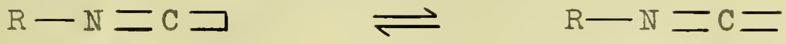
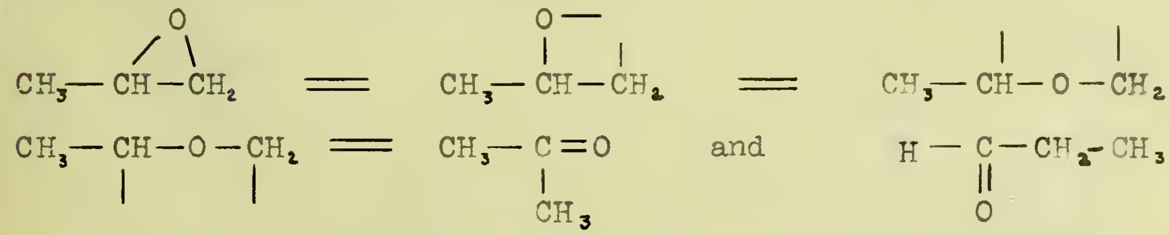
1, 2, 3. Henrich, "Neuere Theoretische Anschauungen auf dem Gebiete der organischen Chemie". Page 239.

Michael so far as the ultimate results are concerned. To explain the excess of free combining energy which Michael has stated molecules possess, Nef introduces the idea of latent valencies which readily dissociate and become active, thus:



(1) (2)

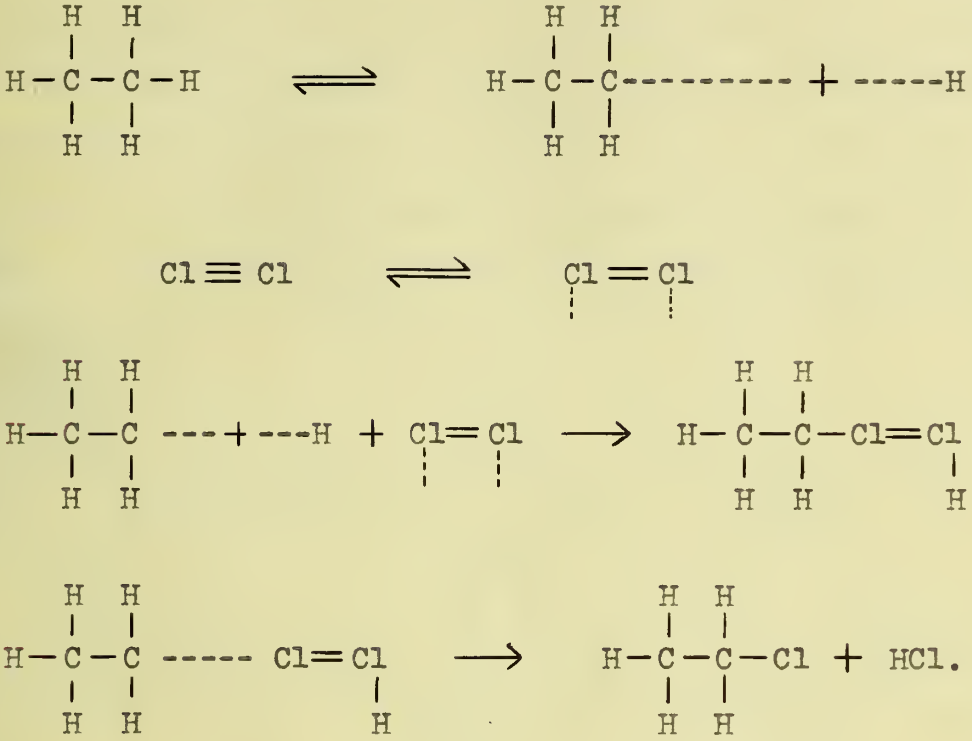
In (1) the latent valencies of the carbon atom polarize each other and the substance is just as inactive and saturated as a member of the paraffin series. But in the form (2) it is very reactive, possessing additive properties common to all unsaturated substances of organic chemistry. Instead of writing the chlorine atom as monovalent Nef, to explain its reactivity, considers it trivalent, so the molecule becomes $Cl\equiv Cl$, and from the above it is evident that in this form it is inactive. To react it must dissociate into the form $Cl=Cl$. But from the recent developments in chemistry, it is evident that form (1) may be coexistent with more or less of form (2). The amount of (2) depends upon the temperature, pressure and concentration. Nef further shows that when propylene oxide is heated with a catalytic substance, dissociation occurs and a hydrogen atom wanders from carbon to carbon, that is, a rearrangement results as follows:



(1) 1/3 yield. (2) 2/3 yield.

The isolation of acetone (1) and the isomeric aldehyde (2) shows that a rearrangement has occurred which Nef attributes to the above

dissociation. In the explanation of the action of chlorine upon ethane, Nef shows a different type of dissociation which will be illustrated by the following:



$$H_3C{-}CH_3 \rightleftharpoons H_3C{-}CH_2{-}{-}{-} + {-}{-}{-}H$$

$$Cl \equiv Cl \rightleftharpoons Cl = Cl$$

$$H_3C{-}CH_2{-}{-}{-}+{-}{-}{-}H + Cl{=}Cl \longrightarrow H_3C{-}CH_2{-}Cl{=}Cl{-}H$$

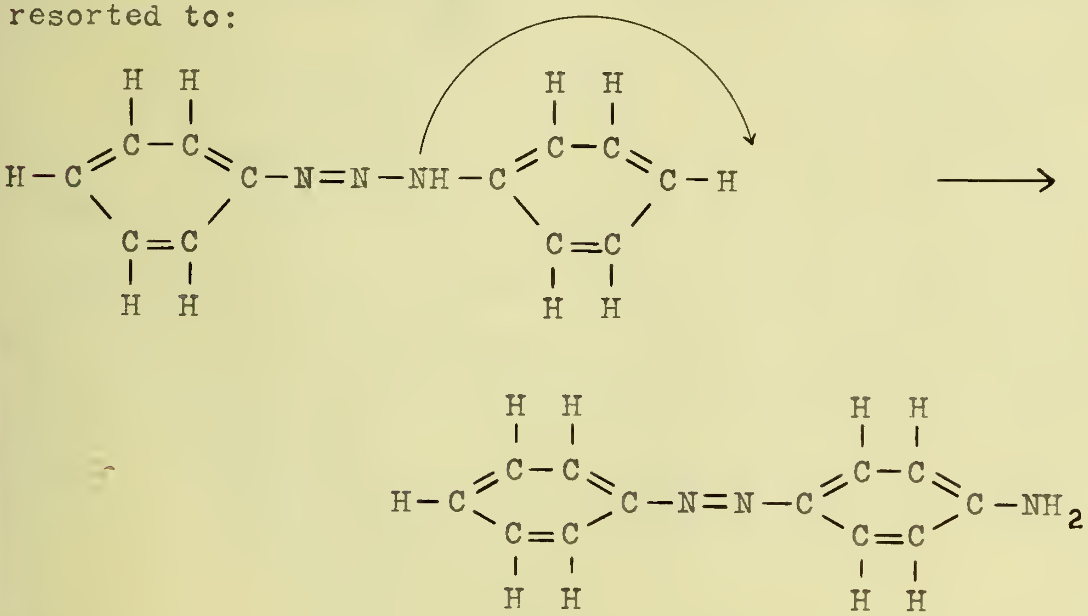
$$H_3C{-}CH_2{-}{-}{-}{-}{-}Cl{=}Cl{-}H \longrightarrow H_3C{-}CH_2{-}Cl + HCl.$$

This illustration gives graphically the gist of Nef's idea. It will be noticed that, in common with Michael , he assumes the formation of an unstable intermediate compound, but offers no reason for its decomposition as did Michael .

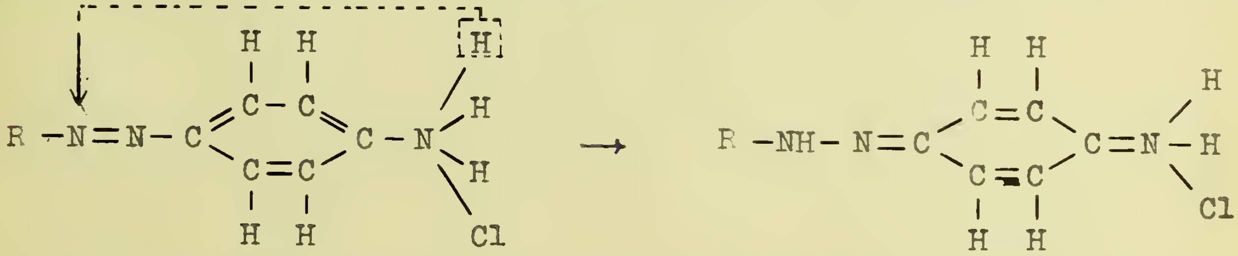
Intimately associated with, and, perhaps, at the basis of the above explanations of the phenomenon of substitution, is the phenomenon of rearrangement. To explain the decomposition of the unstable intermediate product formed by the union of molecules, both Nef and Michael have used the idea of rearrangement. Michael offers a reason why the rearrangement occurs. It is the purpose of this work to bring together the typical rearrangements of organic chemistry and if possible, to offer a reason why they occur and to give some rule as to directions the rearrangement of a given molecule will take. With

this accomplished, the problem of substitution may be attacked in a much more intelligent manner.

The importance of rearrangement in the recent developments of organic chemistry cannot be over estimated, if one stops to consider the important subjects of organic chemistry depending upon this phenomenon for explanation. To mention and illustrate one, that of the cause of color in organic substances, is enough. To explain the change of diazoaminobenzene into aminoazobenzene, rearrangement is resorted to:

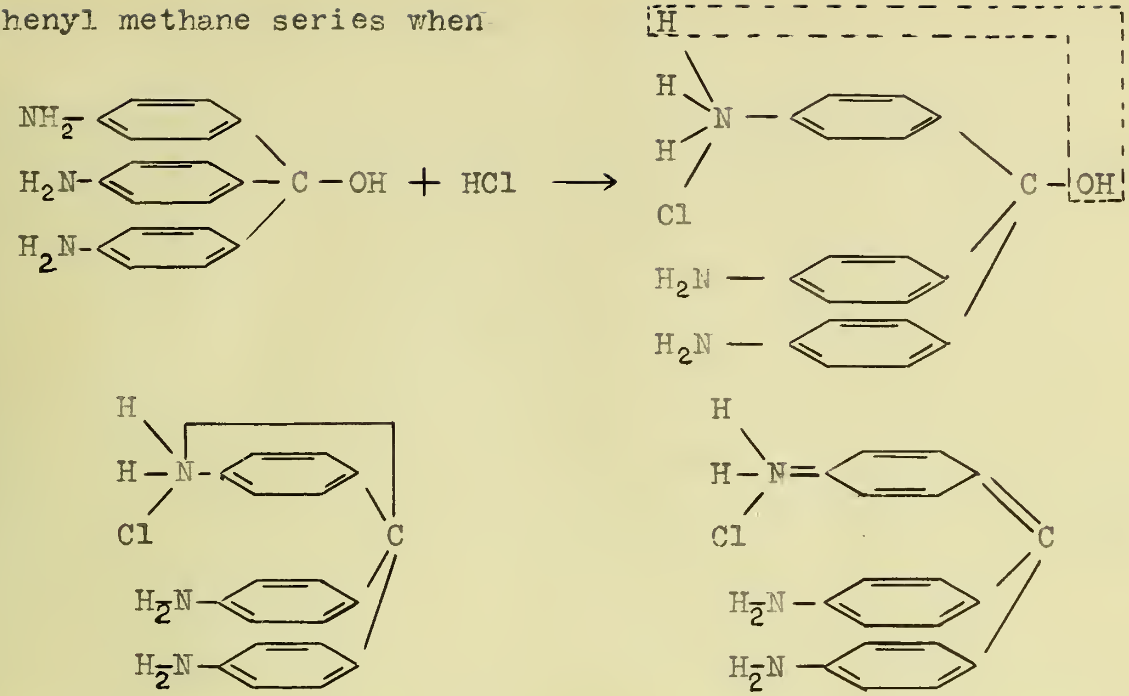


When one stops to consider the importance of this reaction, the need of explanation of rearrangement becomes evident. Further, chemists have been contented to explain the color of the azo dyes as due to the chromophore $-N=N-$. Recent work has shown this to be but partially true for another rearrangement has been found to occur, thus:



This illustration brings to mind the explanation of color in the

triphenyl methane series when

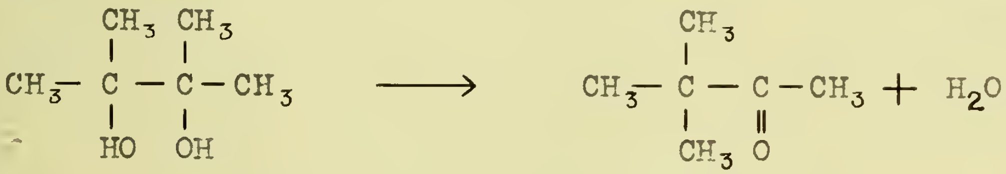


Moreover, the latest theory of color states that this quinoid group is ~~t~~vibrating from one benzene ring to another, involving rearrangement within the molecule which is said to cause the color. So it becomes evident that we should know the laws that rearrangements follow.

SYSTEMIZATION
OF MOLECULAR REARRANGEMENTS.

Very early in the development of organic chemistry it was noted that the substituting group as a whole or in part did not necessarily occupy the same position in the molecule as the group which had been removed. Further, the removal from or the entrance into the molecule of certain atoms might cause the remaining atoms to change position with respect to each other. However, this was considered the exception rather that the rule. This phenomenon is known by different names. In English it is called rearrangement, transposition, etc., while in German it is found under the head of Umlagerung, Umwandlung, etc.

The earliest recorded case of rearrangement was discovered by Fittig in 1860, in which pinacone was changed to pinacoline by the elimination of water. The reaction proceeded as follows:



$$CH_3-\underset{HO}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{O}{\underset{\|}{C}}-CH_3+H_2O$$

Since this discovery the examples have multiplied until Cohen [1] in his recent book has found it necessary to classify rearrangements by type only, giving but a few illustrations of each type.

Theoretical Types of Rearrangements of Organic Compounds.

The fundamental basis of all theories explaining isomerism of organic compounds is the law of the constancy of valence of the carbon atom. Many investigators have recently shown that valence varies with polarity, position in the periodic system, atomic weight, external conditions, etc., but all are united in excepting carbon in organic compounds. Further it is evident to one familiar with or-

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1. J. B. Cohen "Organic Chemistry for Advanced Students".

ganic chemistry that the other elements occurring with carbon usually show a constant valence, or if at all variable only with certain fixed values, as for example, nitrogen is always three or five, never four or six. It may be stated here that the theoretical discussion will be limited to rearrangements occurring between the elements carbon, oxygen and nitrogen. In such rearrangements the valence of carbon will always be four, of oxygen two, and of nitrogen three or five. The valence of oxygen is considered constant because under the conditions where oxonium compounds are formed rearrangements are not likely to occur.

Table I, following, will give the theoretically possible rearrangements between the elements O, N^{III}, N^{V}, and C.

TABLE I.

(1) For rearranging elements or radicals whose valence is	(2) Rearrangements are possible				
	(3) Between elements in open chain			(3′) Between elements in closed chain	
	(4′) United by one valence to open chain, whose	(4^2) United by two valencies to open chain or chains, whose	(4^3) United by three valencies to open chain or chains, whose	(′4′) United by one valence each to two other elements in the ring whose	(^{2}4^2) United by two valencies to one element and one valence to another element in the ring, whose
I	Valence >1 O, N, C.	Valence >2 N, C.	Valence >3 N, C.	Valence >2 N, C.	Valence >3 N, C.
II	Valence >2 N, C.	Valence >3 N, C.	Valence >4 N.	Valence >3 N, C.	Valence >4 N.
III	Valence >3 N, C.	Valence >4 N.		Valence >4 N.	
IV	Valence >4 N.				

Explanation of Tabular Form.

To use the table read under column one (1), then first Roman numeral (I), then two (2), three (3), and finally (4′) or (4^2) or (4^3) as required by the position of the rearranging group and its valence. For a group or element whose valence is two (II), read as before except that the horizontal column headed by the valence value two (II) should be read instead of that headed by the valence value one (I) as first directed, etc. For rearrangements between elements in the closed chain, substitute column three prime (3′) for three (3) and follow the same rule as under three (3) except that (4′), (4^2), and (4^3) are substituted by (′4′) and (^{2}4^2). Illustration: For rearranging elements or groups whose valence is one (I), rearrangements are possible between elements in the open

chain (united by one valence to the open chain) whose valence is greater than one (I), that is, between oxygen (O), nitrogen (N), and carbon (C).

A table discussing the theoretical rearrangements between the side chain and the ring or vice-versa is unnecessary since these cases are covered by the discussion under column three prime (3').

Classes of Known Rearrangements.

With the facts of Table I in mind, Table II has been arranged to show the present state of the problem of rearrangement. In the first vertical column, a partial list of the elements and radicals has been given. In the first horizontal row is given the elements between which the rearrangement occurs; while the second horizontal row gives their position in the compound, that is whether in the ring or side chain. The third row gives the class to which each rearrangement of a given group is assigned. In the first horizontal row the letter stands for the atomic symbol of the element and the arrow shows the direction of the rearrangement. In the second row Op stands for ppen chain, R for closed chain or ring, Op→R for open or side chain to closed chain, and R→Op from closed to open or side chain. Thus to read the behavior of the alkyl group for class I, it is evident that the alkyl group will rearrange from carbon to carbon in the open chain; or for class 8, it is evident that the alkyl group may rearrange from carbon in the ring to oxygen in the side chain. Those rearrangements which are theoretically impossible because of the law of constant valence of organic chemistry are designated by the sign X, while those impossible for the trivalent but possible for the pentavalent nitrogen are designated by the sign V.

To show the present state of knowledge of the phenomenon of rearrangement , the following system of marking is employed in the vertical columns beneath the classes:

O designates occasional occurrence.

C designates common occurrence.

r designates rare occurrence.

Doubtless the above scheme is incomplete so far as the known cases are concerned but it must be borne in mind that such a table when completed will demand many years of careful reading, especially in a field where systemization has not been attempted.

Element or Group.	→ N		$O_p \rightarrow R$				$R \rightarrow O_p$				$R \rightarrow R$				
	O_p ↓ R	R ↓ O_p	C	C ↓ O	C ↓ N	C O N	C	C ↓ O	C ↓ N	C O N	C	C C O	C ↓ N	C O N	
Class.	5	36	37	38	39	40	41	42	43	44	45	46	47	48	
Alkyl			c	c	c						c				
Arryl															
Acyl															
Arcyl															
Hydroxyl															
Oxalkyl															
Oxarryl															
Aldehyde															
Carbonyl															
Carboxyl															
Carboxalkyl															
Carboxarryl															
Amine															
Alkylamine															
Arrylamine															
Nitro															
Nitroso															
Isonitroso	v	v													
Hydrogen															
Halogens															
Sulphonic															
Double Union															

TABLE II.

Element or Group.	C → C				C → O				O → C				C → N				N → C				O → O				O → N				N → O				N → N				O_p → R				R → O_p				R → R			
	O_p	R	$O_p \downarrow R$	$R \downarrow O_p$	O_p	R	$O_p \downarrow R$	$R \downarrow O_p$	O_p	R	$O_p \downarrow R$	$R \downarrow O_p$	O_p	R	$O_p \downarrow R$	$R \downarrow O_p$	O_p	R	$O_p \downarrow R$	$R \downarrow O_p$	O_p	R	$O_p \downarrow R$	$R \downarrow O_p$	O_p	R	$O_p \downarrow R$	$R \downarrow O_p$	O_p	R	$O_p \downarrow R$	$R \downarrow O_p$	O_p	R	$O_p \downarrow R$	$R \downarrow O_p$	C	$C \downarrow O$	$C \downarrow N$	C O N	C	$C \downarrow O$	$C \downarrow N$	C O N	C	C C O	$C \downarrow N$	C O N
Class.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
Alkyl	o	o	o	o		x	x		o	x		x					c	c				x	x	x	c	x		x		x	x						c	c	c						c			
Arryl	c					x	x			x		x	c									x	x	x		x		x		x	x																	
Acyl						x	x		o	x		x							c			x	x	x	o	x		x		x	x																	
Arcyl						x	x		o	x		x							o			x	x	x	o	x		x		x	x																	
Hydroxyl						x	x			x		x							c			x	x	x		x		x		x	x																	
Oxalkyl						x	x			x		x										x	x	x		x		x		x	x																	
Oxarryl						x	x			x		x										x	x	x		x		x		x	x																	
Aldehyde						x	x			x		x										x	x	x		x		x		x	x																	
Carbonyl						x	x			x		x										x	x	x		x		x		x	x																	
Carboxyl						x	x			x	r	x										x	x	x		x		x		x	x																	
Carboxalkyl						x	x			x		x										x	x	x	r	x		x		x	x																	
Carboxarryl						x	x			x		x										x	x	x		x		x		x	x																	
Amine						x	x			x		x							c			x	x	x		x		x		x	x																	
Alkylamine						x	x			x		x										x	x	x		x		x		x	x																	
Arrylamine						x	x			x		x							c			x	x	x		x		x	c	x	x																	
Nitro						x	x			x		x							o			x	x	x		x		x		x	x																	
Nitroso						x	x			x		x							o			x	x	x		x		x		x	x																	
Isonitroso					x	x	x	x	x	x	x	x		v	v			v		v	x	x	x	x	x	x	x	x	x	x	x	x		v	v	v												
Hydrogen	c	c		c	c	x	x	c	c	x	o	x	c	c	c	c	c	c	c	c	c	x	x	x		x		x		x	x																	
Halogens						x	x			x		x							c			x	x	x		x		x	o	x	x																	
Sulphonic						x	x			x		x						o	c			x	x	x		x		x		x	x																	
Double Union	c	c	c	c	c	x	x	c	c	x	c	x	c	c	c	c	c	c	c			x	x	x	c	x		x	c	x	x																	

CAUSE OF THE
PHENOMENON OF REARRANGEMENT.

Speed of Reaction vs. Stability.

Nernst[1], while discussing reaction velocity and temperature in his text book makes the following statement,"Der Umstand, dass in chemischen Systemen die Reaktionsgeschwindigkeit sehr häufig ganz ausserordentlich klein ist, trotzdem dieselben weit vom Gleichgewichte entfernt sind, besitzt fur unsere Kenntnis der chemischen Verbindungen die allergrösste Wichtigkeit. Die grosse Mehrzahl aller organischen Verbindungen hätten niemals das Licht der Welt erblickt, wenn sie mit grosser Geschwindigkeit in den stabileren Zustand übergingen. Die vielen polymeren Kohlenwasserstoffe der Formel C_nH_n könnten gleichzeitig gar nicht existieren, wenn sie alle sofort in das System, das der grössten Stabilität und der Formel C_nH_n entspricht, übergingen; dass gerade die organische Chemie recht eigentlich das Gebiet der im obigen Sinne instabilen Verbindungen ist, die aber dabei in messbarer Zeit äusserst langsam oder überhaupt nicht in beständigere Formen übergehen, findet in der Trägheit der Kohlenstoffbindung (S. 294) ihre Erklärung.

Chemische Systeme, die von der stabilen Form weit entfernt sind, verändern sich häufig bei Temperatursteigerung, wenn diese nämlich der Geschwindigkeit, mit der sie dem Gleichgewichtszustande zustreben, einen hinreichenden Wert erteilt. Man denke an die unzähligen Zersetzungen, Verkohlungen, Verpuffungen u. s. w. organischer Verbindungen beim Erhitzen, an die Verbrennungen vieler Stoffe im Sauerstoff u. s. w. In den meisten dieser Fälle beschleunigt die Erwärmung nur eine Reaktion, sei es eine Zersetzung, sei es eine Verbindung, die nach hinreichend langer Zeit, die freilich häufig z. B. nach vielen Jahrtausenden zahlen dürfte, auch von selbst vor

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[1] W. Nernst - Theoretische Chemie p. 670.

sich gegangen wäre. Ist einmal durch Erwärmung die Umwandlung vollzogen, so kann sie natürlich bei Abkühlung nicht wieder rückgängig werden, weil das System sich nach Abkühlung in einem stabileren Zustande befindet wie vorher. Hierdurch erklärt sich die Existenz der vielen nicht umkerhrbaren Zersetzungen, die wesentlich von den eigentlichen Dissoziationserscheinungen verschieden sind, sowie diejenige der vielen nur in einem Sinne verlaufenden Reaktionen."

Classification of Rearrangements.

From the above quotations it is evident that in rearrangements the question of stability is paramount. But before it can be considered, rearrangements must be classified. In a review of a majority of the known cases , it is clear that certain transformations are possible only because some atoms have been added to or taken away from the original molecule. Such rearrangements will be termed rearrangements with reactions. On the other hand the true transposition occurs without the addition or subtraction of other atoms to or from the original molecule. It consists essentially in a rearrangement of the atoms already present. Such rearrangements will be termed rearrangements without reactions or true rearrangements.

Chemists believe that,theorectically,a given compound may be coexistent with its decomposition products or isomers. For example,sulphur trioxide is supposed to exist in the form $SO_3 \rightarrow S + 3O$. The concentration of the decomposition products may be so small at ordinary temperature as to escape detection, yet in most cases increased temperature will reveal them. So with rearrangements, the original compound must be slowly changing into its isomer (the product resulting from rearrangement) even

though it cannot be detected. But in many cases an equilibrium can easily be detected as for example in the phenomenon of tautomerism. In such cases the equilibrium is reversible while in many others the reaction appears to be non-reversible, as for example,

$CH_3-CH_2-CH=CH-CH_2 COOH$ Δ^2 Hexenic acid $CH_3 CH_2 CH_2 CH=CH-COOH$ Δ^1 Hexenic acid.

Hence rearrangements must be further divided into the classes of

(1) Reversible reactions.

(2) Non-reversible reactions.

Again, the above quotation makes the life of a given compound dependent upon the speed of reaction with which it is changing into its more stable isomers or decomposition products. It is a well known fact that reactions of inorganic chemistry proceed with much greater velocity than those of organic chemistry, as is well illustrated by the rate at which silver iodide will be precipitated from potassium iodide and methyl iodide. For this reason many reactions of inorganic chemistry have been investigated successfully only after substituting an organic radical into the molecule, as for example the recent work on Caro's Reagent.

Also it is a well known fact that reactions in the aromatic series proceed with less velocity than those in the aliphatic series of organic chemistry. This is well illustrated by the fact that the diazonium compounds of the aromatic series are unknown in the aliphatic series, where nitrous acid instead of giving diazonium hydroxide or derivatives gives a hydroxyl compound when acting upon a primary amine. Also, the establishment of the position of the replaceable hydrogen in nitromethane became possible when phenylnitromethane was studied because the speed of reaction was decreased by the presence of the phenyl group so that the two isomeric forms could be isolated. Hence it

becomes evident that Nernst's relation of stability with reaction velocity is of fundamental importance in the study of the phenomenon of rearrangement.

Further, rearrangements generally take place in the presence of of certain reagents. It is of fundemental importance to determine the influence of these reagents upon this phenomenon. In the majority of cases, it has been found that acids rearrange basic compounds and that bases rearrange acidic compounds. From the previous discussion it is evident that the compound, which suffers rearrangement, is slowly changing into a more stable form in the absence of these reagents, while in the presence of these reagents the rearrangement is completed in a short time. That is, these reagents must be catalytic to the rate of the rearrangement. Thus the hydrogen ion is catalytic to basic and the hydroxyl ion to acidic rearrangements. "Beckmann[1] expressed a similar view in reference to the reaction that bears his name. Goldschmidt and Reinders[2] in the case of diazoaminobenzene showed that the velocity of isomeric change from diazoaminobenzene to aminoazobenzene increased with the proportion of the catalyst (an anilin salt) and with the dissociation constant."

It is the purpose of the following discussion to show that all true rearrangements of the so-called non-reversible type do proceed in the direction to produce more stable compounds when catalyzed by acids, bases, etc. Since reaction velocity may also be increased by temperature, pressure, ions in general and other substances it follows that these factors will catalyze rearrangements

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1. Beckmann- Berichte 27 - 300 - (1894) .
2. Goldschmidt and Reinders - Berichte 29 - 1369, 1899 (1896).

and must be considered. A study of the order of such reactions should be made whenever possible.

Chemical Stability.

Since the existence or stability of a given organic compound is dependent upon the smallness of the reaction velocity with which it is changing into a more stable form, it is evident that a measure of both reaction velocity and chemical stability should be found. Reaction velocity is easily determined by the amount of the substance formed in a given time.

Chemical stability has been measured by different methods depending upon the observer. Abegg in his recent work upon valence makes the resistivity of compounds toward heat a measure of their stability. Inorganic chemists point to the argon group as the typically stable elements, while organic chemists unite in stating that the paraffins are the most stable of all organic compounds. The word paraffin means without affinity and thus the resistivity of a compound to chemical change has been taken as a measure of its chemical stability.

The recent developments of thermodynamics have made it possible for chemists to express many properties in terms of energy. So in this case energy has been applied as a measure of chemical stability. Berthelot [1] advanced the theorem in 1867 that " every chemical change gives rise to the production of those substances which occasion the greatest development of heat." Hence the total energy of a compound was taken as the measure of its chemical stability. This principle was finally over thrown. The following illustration shows its fallacy. Given a volume of a perfect gas at a definite temperature and pressure. Allow it to expand into a vacuum when it does no work since there is no resistance acting against it.

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1. Nernst - Theoretische Chemie - Sechste Auflage - 29, 691.

Since there has been no change in the total energy of the gas during this operation it is evident that the total energy is not a measure of the stability of such a system.

The capacity of the above gaseous system to do work was decreased by the expansion. This capacity for doing work or the free energy of the system is, however, taken as a measure of chemical stability [1]. In the following tables and discussions the free energy of ionization will be chosen as the measure of chemical stability. The affinity constant (K) is chosen as a measure of stability since from the second law of thermodynamics the expression $A = RT\ln K$ is obtained in which A is the free energy of ionization, R is the gas constant, T is the absolute temperature and K is the affinity constant. Hence the free energy of ionization is proportional to the natural logarithm of the affinity constant and since that substance is the most stable which contains the smallest amount of free energy of ionization, the natural logarithm of its affinity constant must have a minimum value. If rearrangements of acids and bases take place in the direction to decrease the free energy of ionization, that is, to increase their stability, then this may be proven from a study of their ionization constants which will be furnished by the following tables and curves.

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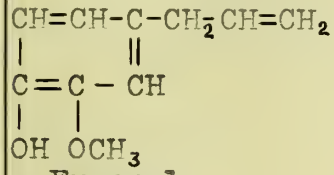
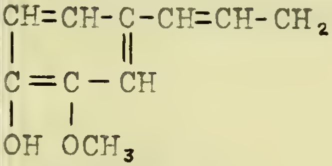
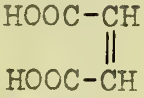
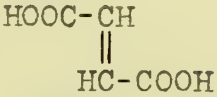
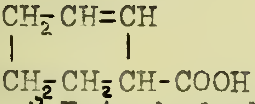
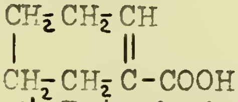
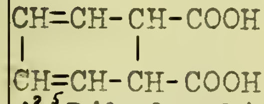
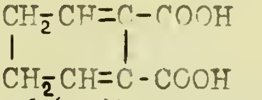
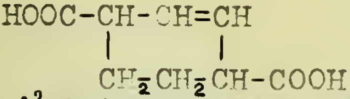
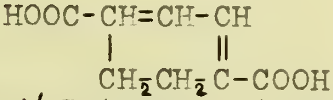
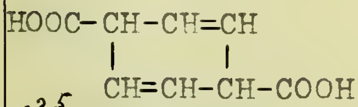
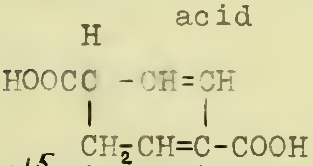
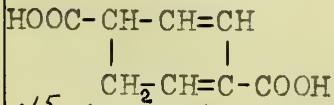
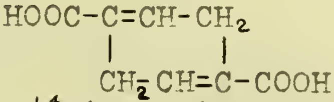
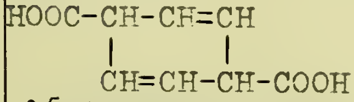
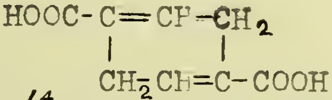
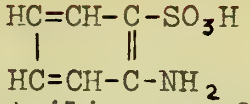
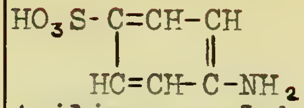
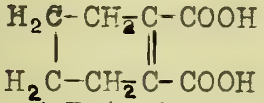
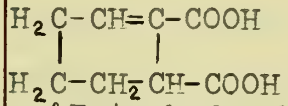
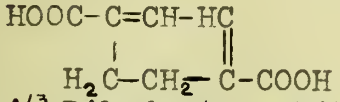
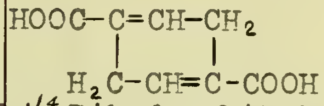
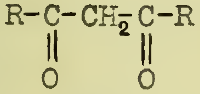
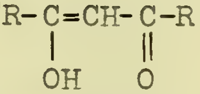
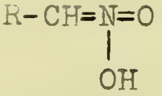
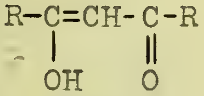
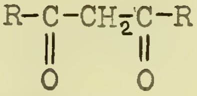
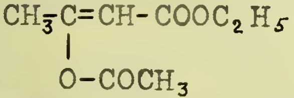
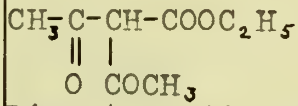
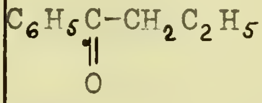
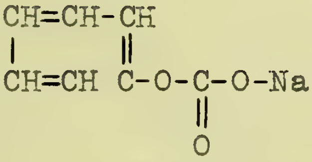
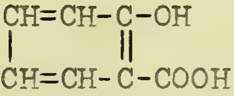
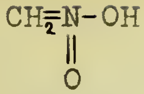
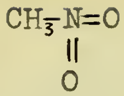
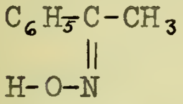
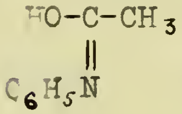
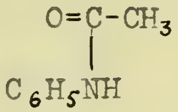
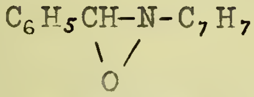
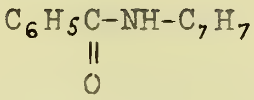
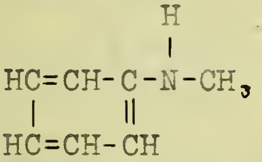
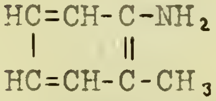
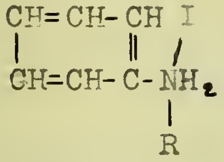
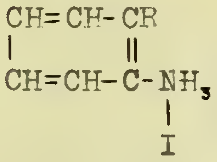
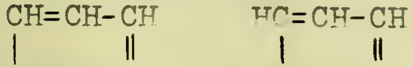
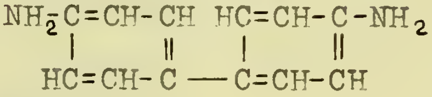
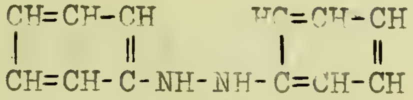
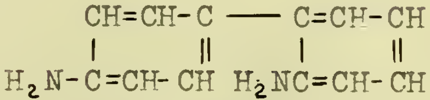
[1] Nernst - Theoretische Chemie- Sechste Auflage - 29, 691.

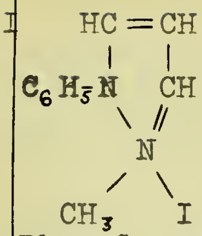
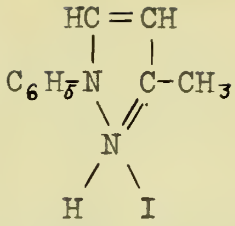
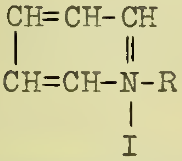
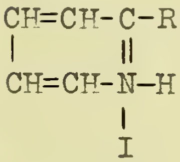
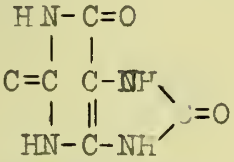
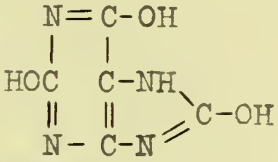
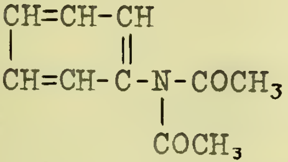
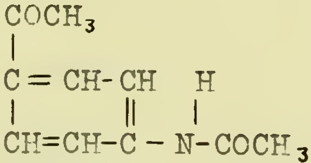
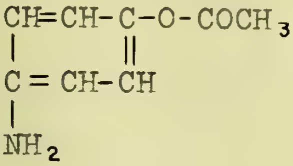
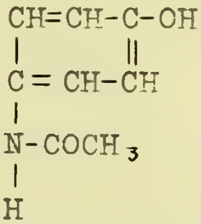
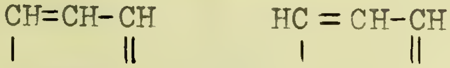
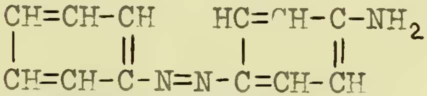
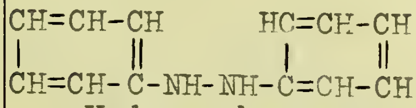
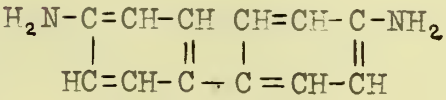
TABLE III.

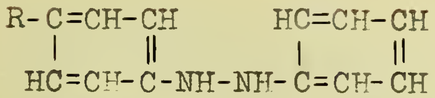
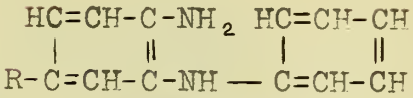
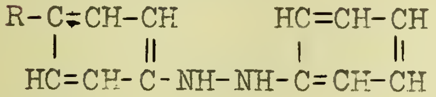
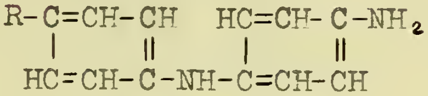
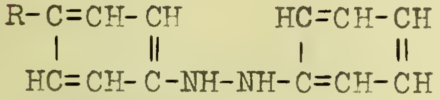
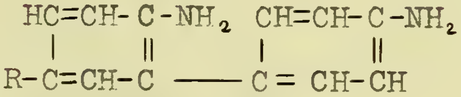
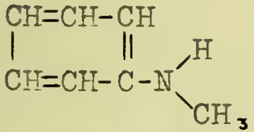
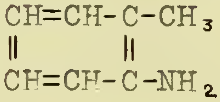
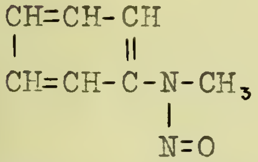
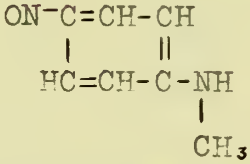
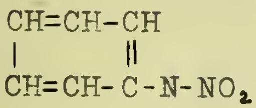
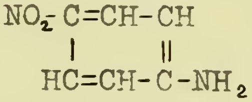
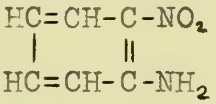
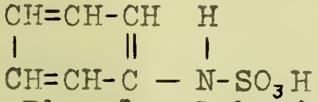
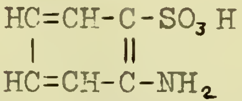
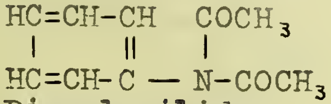
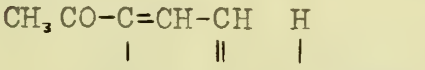
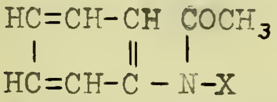
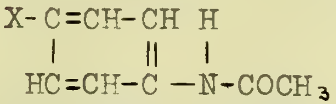
Classification of True Rearrangements According to Classes of Table II.

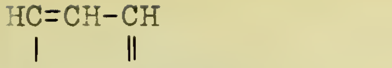
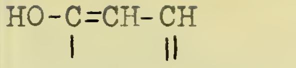
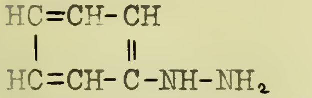
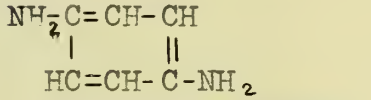
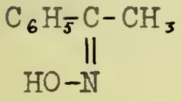
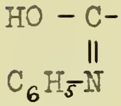
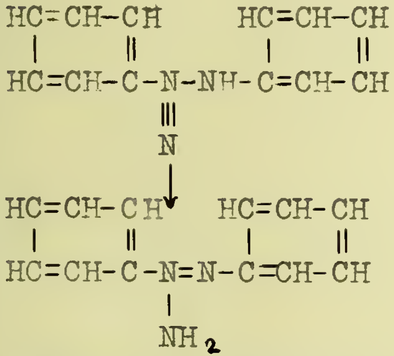
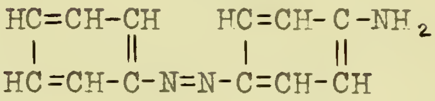
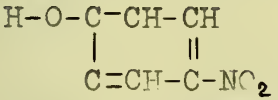
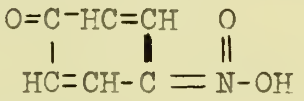
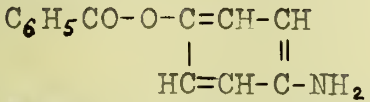
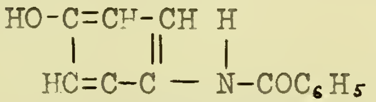
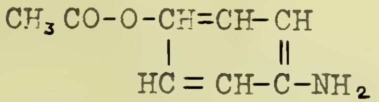
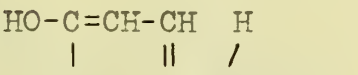
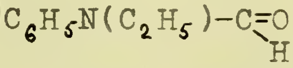
Class	True Rearrangements		Catalyzer
	Before.	After.	
I	$CH_3{-}CH_2{-}CH{=}CH{-}CH_2COOH$ Dihydrosorbic acid	$CH_3{-}CH_2{-}CH_2{-}CH{=}CH{-}COOH$ Δ' Hexenic acid.	OH $^-$
	 $\begin{array}{l} CH{=}CH{-}C{-}CH_2CH{=}CH_2 \\ \vert \qquad\quad \Vert \\ C{=}C{-}CH \\ \vert \quad \vert \\ OH\ OCH_3 \end{array}$ Eugenol	 $\begin{array}{l} CH{=}CH{-}C{-}CH{=}CH{-}CH_2 \\ \vert \qquad\quad \Vert \\ C{=}C{-}CH \\ \vert \quad \vert \\ OH\ OCH_3 \end{array}$ Isoeugenol	OH $^-$
	(2)  $\begin{array}{l} HOOC{-}CH \\ \qquad\quad \Vert \\ HOOC{-}CH \end{array}$ Maleic acid	 $\begin{array}{l} HOOC{-}CH \\ \qquad\quad \Vert \\ \qquad HC{-}COOH \end{array}$ Fumaric acid	Heat H^+at 25° Pressure
II	 $\begin{array}{l} CH_2{-}CH{=}CH \\ \vert \qquad\quad \vert \\ CH_2{-}CH_2{-}CH{-}COOH \end{array}$ Δ^2 Tetrahydrobenzoic acid	 $\begin{array}{l} CH_2{-}CH_2{-}CH \\ \vert \qquad\qquad \Vert \\ CH_2{-}CH_2{-}C{-}COOH \end{array}$ Δ' Tetrahydrobenzoic acid	OH $^-$
	 $\begin{array}{l} CH{=}CH{-}CH{-}COOH \\ \vert \qquad\quad \vert \\ CH{=}CH{-}CH{-}COOH \end{array}$ $\Delta^{2,5}$ Dihydrophthalic acid	 $\begin{array}{l} CH_2{-}CH{=}C{-}COOH \\ \vert \qquad\quad \vert \\ CH_2{-}CH{=}C{-}COOH \end{array}$ $\Delta^{2,6}$ Dihydrophthalic acid	OH $^-$
	 $\begin{array}{l} HOOC{-}CH{-}CH{=}CH \\ \qquad\ \vert \qquad\ \vert \\ \qquad CH_2{-}CH_2{-}CH{-}COOH \end{array}$ Δ^2 Tetrahydro Terephthalic acid	 $\begin{array}{l} HOOC{-}CH{=}CH{-}CH \\ \qquad\ \vert \qquad\ \Vert \\ \qquad CH_2{-}CH_2{-}C{-}COOH \end{array}$ Δ' Tetrahydroterephthalic acid	OH $^-$
	 $\begin{array}{l} HOOC{-}CH{-}CH{=}CH \\ \qquad\ \vert \qquad\ \vert \\ \qquad CH{=}CH{-}CH{-}COOH \end{array}$ $\Delta^{2,5}$ Dihydroterephthalic acid	 $\begin{array}{l} HOOC\overset{H}{C}{-}CH{=}CH \\ \qquad\ \vert \qquad\ \vert \\ \qquad CH_2{-}CH{=}C{-}COOH \end{array}$ $\Delta^{1,5}$ Dihydroterephthalic acid	OH $^-$
	 $\begin{array}{l} HOOC{-}CH{-}CH{=}CH \\ \qquad\ \vert \qquad\ \vert \\ \qquad CH_2{-}CH{=}C{-}COOH \end{array}$ $\Delta^{1,5}$ Dihydroterephthalic acid	 $\begin{array}{l} HOOC{-}C{=}CH{-}CH_2 \\ \qquad\ \vert \qquad\ \vert \\ \qquad CH_2{-}CH{=}C{-}COOH \end{array}$ $\Delta^{1,4}$ Dihydroterephthalic acid	OH $^-$
	 $\begin{array}{l} HOOC{-}CH{-}CH{=}CH \\ \qquad\ \vert \qquad\ \vert \\ \qquad CH{=}CH{-}CH{-}COOH \end{array}$ $\Delta^{2,5}$ Dihydroterephthalic acid	 $\begin{array}{l} HOOC{-}C{=}CH{-}CH_2 \\ \qquad\ \vert \qquad\ \vert \\ \qquad CH_2{-}CH{=}C{-}COOH \end{array}$ $\Delta^{1,4}$ Dihydroterephthalic acid.	OH $^-$

	 Aniline-o-sulphonic acid	 Aniline-p-sulphonic acid	H_2SO_4 Heat
	 Δ′ Tetrahydrophthalic acid	 Δ² Tetrahydrophthalic acid	OH^-
	 Δ^1,3 Dihydroterephthalic acid	 Δ^1,4 Dihydrophthalic acid	OH^-
V	 $R-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-R$ Keto --- Malonic ester	 $R-\underset{OH}{\underset{\|}{C}}=CH-\underset{O}{\underset{\|}{C}}-R$ -- Enol	OH^-
	$R-CH_2-NO_2$ Nitro compound	 $R-CH=\underset{OH}{\underset{\|}{N}}=O$ Iso nitro compound	OH^-
IX	 $R-\underset{OH}{\underset{\|}{C}}=CH-\underset{O}{\underset{\|}{C}}-R$ Enol ----- Tautomerism	 $R-\underset{O}{\underset{\|}{C}}-CH_2-\underset{O}{\underset{\|}{C}}-R$ --Keto	H^+
	 $CH_3-\underset{O-COCH_3}{\underset{\|}{C}}=CH-COOC_2H_5$ Acetohydroxycrotonic ester	 $CH_3-\underset{O}{\underset{\|}{C}}-\underset{COCH_3}{\underset{\|}{CH}}-COOC_2H_5$ Diacetoacetic ester	$NaOOCCH_3$ Acetic anhydride
	$C_6H_5C(OC_2H_5)=CH_2$ Isoacetophenone ethylether	 $C_6H_5\underset{O}{\underset{\|}{C}}-CH_2C_2H_5$ Phenyl-propylketone	Boiling under pressure
XI	 Sodium Phenyl Carbonate	 Salicylic acid	Heat

XIII	 $CH_2=\underset{\underset{\displaystyle O}{\Vert}}{N}-OH$ Isonitro methane	 $CH_3-\underset{\underset{\displaystyle O}{\Vert}}{N}=O$ Nitro methane	OH^-
	$N\equiv C-CH_2-COOC_2H_5$ Cyanacetic ester	$HN=C=CH-COOC_2H_5$ Enolcyanacetic ester	NaOR
	 $C_6H_5-\underset{\underset{\displaystyle H-O-N}{\Vert}}{C}-CH_3$ Phenyl methyl ketoxime	 $HO-\underset{\underset{\displaystyle C_6H_5N}{\Vert}}{C}-CH_3$ Intermediate  $O=\underset{\underset{\displaystyle C_6H_5NH}{\vert}}{C}-CH_3$ Acetanilide	H^+ Acid-chlorides PCl_5 $\begin{matrix}CH_3CO\\CH_3CO\end{matrix}\!>O$ P_2O_5
XVI	 $C_6H_5\underset{\diagdown\ \diagup}{\overset{}{CH-N}}-C_7H_7$ with O below Benzaloxim Benzyl	 $C_6H_5\underset{\underset{\displaystyle O}{\Vert}}{C}-NH-C_7H_7$ Benzyl benzamide	PCl_5 $POCl_3$
	 $\begin{array}{l}\qquad\qquad\ \ H\\ \qquad\qquad\ \ \vert\\ HC=CH-C-N-CH_3\\ \vert\qquad\quad\ \Vert\\ HC=CH-CH\end{array}$ Methyl aniline	 $\begin{array}{l}HC=CH-C-NH_2\\ \vert\qquad\quad\ \Vert\\ HC=CH-C-CH_3\end{array}$ o-Toluidine	Heat
	 $\begin{array}{l}CH=CH-CH\ \ I\\ \vert\qquad\quad\ \Vert\ \ /\\ CH=CH-C-NH_2\\ \qquad\qquad\quad\ \vert\\ \qquad\qquad\quad\ R\end{array}$ Alkyliodide of anilin	 $\begin{array}{l}CH=CH-CR\\ \vert\qquad\quad\ \Vert\\ CH=CH-C-NH_3\\ \qquad\qquad\quad\ \vert\\ \qquad\qquad\quad\ I\end{array}$ Anilinhydroiodide	Heat
	Benzidine  $\begin{array}{l}CH=CH-CH\qquad\qquad\quad HC=CH-CH\\ \vert\qquad\quad\ \Vert\qquad\qquad\qquad\ \vert\qquad\quad\ \Vert\\ CH=CH-C-NH-NH-C=CH-CH\end{array}$ Hydrazobenzene	Rearrangements.  $\begin{array}{l}NH_2C=CH-CH\ \ HC=CH-C-NH_2\\ \quad\ \vert\qquad\ \Vert\qquad\ \vert\qquad\quad\ \Vert\\ \quad\ HC=CH-C-C=CH-CH\end{array}$ Benzidine	H^+
	Ortho Semidine	Rearrangement	
	Para Semidine	Rearrangement	
	 $\begin{array}{l}CH=CH-CH\qquad\qquad\quad HC=CH-CH\\ \vert\qquad\quad\ \Vert\qquad\qquad\qquad\ \vert\qquad\quad\ \Vert\\ CH=CH-C-NH-NH-C=CH-CH\end{array}$ Hydrazo Benzene	 $\begin{array}{l}\quad\ CH=CH-C-C=CH-CH\\ \quad\ \vert\qquad\quad\ \Vert\qquad\ \vert\qquad\quad\ \Vert\\ H_2N-C=CH-CH\ \ H_2NC=CH-CH\end{array}$ Diphenyl base.	H^+
XVII	$R-N=C$ Alkyl Isocyanide	$R-C\equiv N$ Alkyl Cyanide	Heat

XVIII	 Phenyl pyrazole methyl iodide.	 Phenyl methyl pyrazole hydroiodide.	Heat 250-350°.
	 Alkyl pyridinium iodides	 Alkyl pyridines	Heat
	Uric acid.	Group tautomerism.	
	 Keto form.	 Enol form.	
XIX	 Diacet anilide	 p-aceto-acetanilide	Zn Cl_2 probably H^+ from hydrolysis.
	 p-Amino acetophenol	 p-hydroxyacetanilide.	OH^-
	 Diazoamino compound	 Aminoazo dyes.	Hydrochloride of amine.
	Benzidine	Rearrangements.	
	 Hydrazo benzene.	 Benzidine	H^+

	Ortho semidine  p-Alkyl hydrazo benzene	Rearrangements.  ortho semidine.	H^+
	Para Semidine  p-Alkyl hydrazo benzene	Rearrangements.  para semidine.	H^+
	 p-Alkyl hydrazo benzene	 Diphenyl base.	H^+
	 Methyl aniline	 Toluidine.	Heat.
	 Nitroso amine of mono methyl aniline	 p-Nitroso methyl aniline.	H Cl in alcohol
	 Phenyl nitramine	 p-Nitr-anilin  o-Nitr-anilin.	H^+
	 Phenyl sulphamic acid	 Aniline-o-sulphonic acid.	H^+ Acetic & drop of H_2SO_4
	 Diacylanilide	 p-acet-acetanilide	$ZnCl_2$ Probably H^+ from Hydrolysis
XIX	 Acylhaloanilides	 p-Halogen acetanilides.	Glacial acetic acid.

	 Phenyl hydroxylamine	 p-Hydroxyanilin	Mineral acid. H^+
	 Phenyl hydrazine	 p-Phenylenediamine.	Strong H Cl at 200° H^+
	Beckman	Rearrangements.	
	 Acetophenone oxime	 Iso acetophenon oxime.	Strong acid $POCl_3$ PX_5 PX_3 P_2O_5 Acetic anhydrides.
	 Diazoamino benzene	 Amino azo benzene.	Hydrochloride of amine Probably H^+ from hydrolysis
XXI	 p-Nitro phenol	 Quinoid p-nitro phenol.	
XXV	 Benzoyl p-hydroxyaniline	 p-hydroxy-benzol acetanilide.	OH^-
	 Acetyl p-hydroxyaniline	 p-hydroxy-acetanilide.	OH^-
	$NH_2C_6H_5O-COOC_2H_5$ Amino phenyl carbonate.	$C_2H_5OOC-NH-C_6H_5OH$ Phenol methane.	
	$C_6H_5N=CHOC_2H_5$ Imino ether of formanilide	 $C_6H_5N(C_2H_5)-\overset{}{C}\underset{H}{=}O$ Ethyl formaniline.	Heat 200°

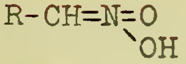
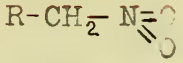
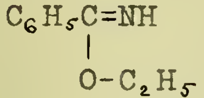
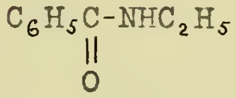
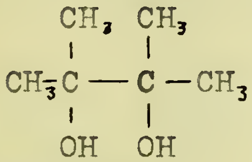
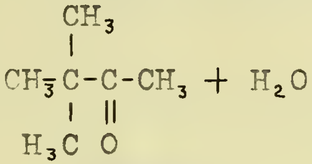
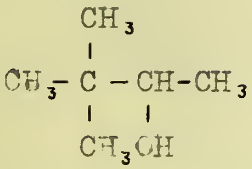
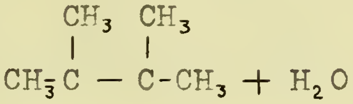
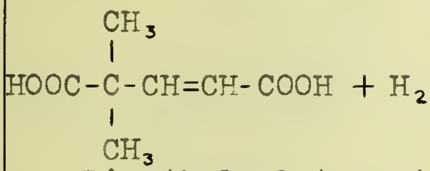
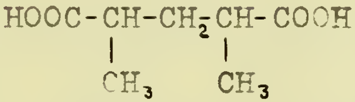
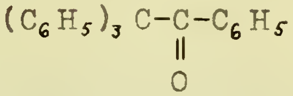
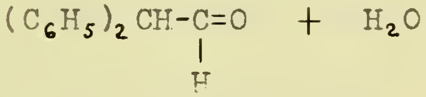
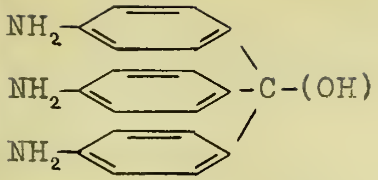
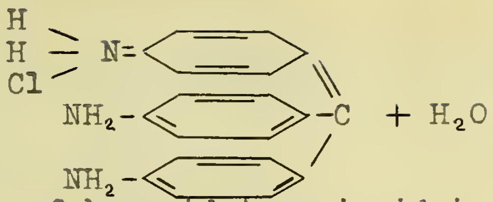
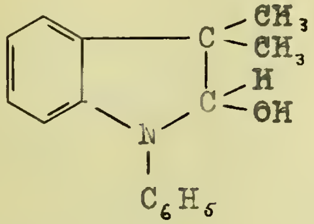
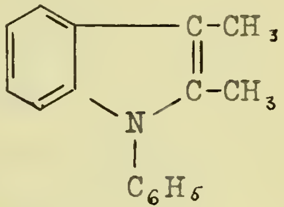
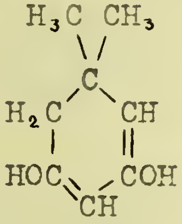
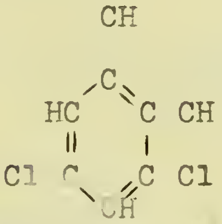
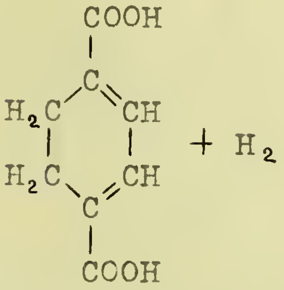
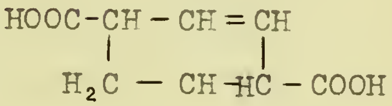
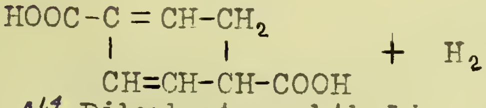
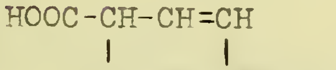
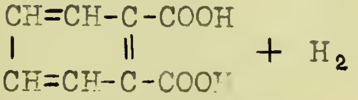
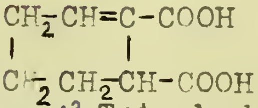
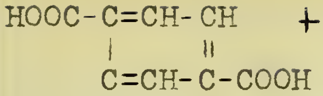
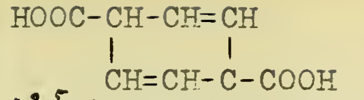
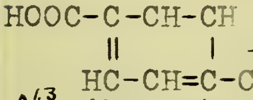
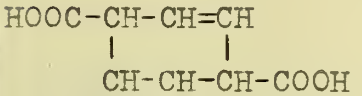
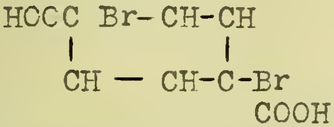
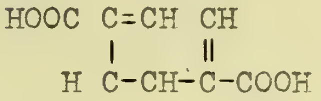
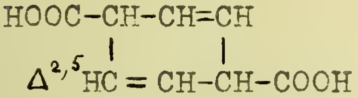
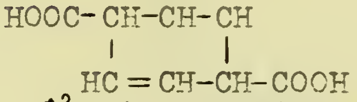
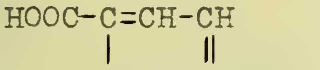
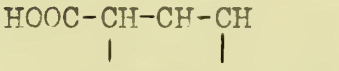
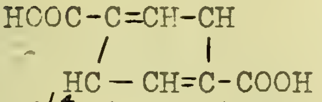
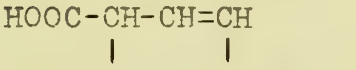
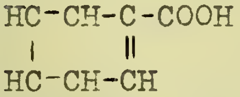
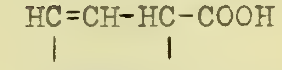
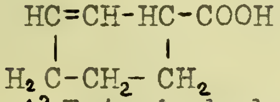
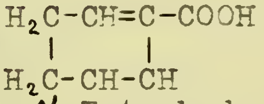
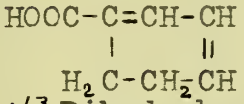
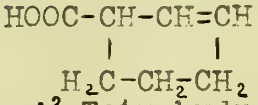
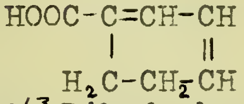
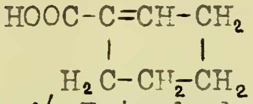
	 $R-CH=N\begin{smallmatrix}=O\\ \diagdown OH\end{smallmatrix}$ Isonitro compound	 $R-CH_2-N\begin{smallmatrix}=O\\ \diagdown O\end{smallmatrix}$ Nitro compound.	H^+
	 $C_6H_5\underset{\underset{O-C_2H_5}{\vert}}{C}=NH$ Benzimidoethyl ether	 $C_6H_5\underset{\underset{O}{\Vert}}{C}-NHC_2H_5$ Ethyl amino benzoic acid.	Heat alome or with R X
	$R-O-C\equiv N$ Cyanic ester.	$R-N=C=O$ Isocyanic ester.	Heat

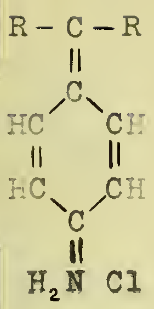
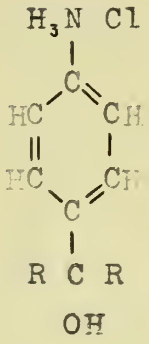
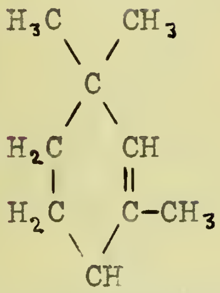
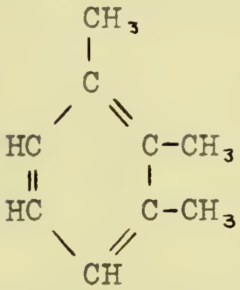
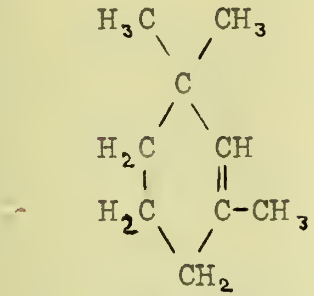
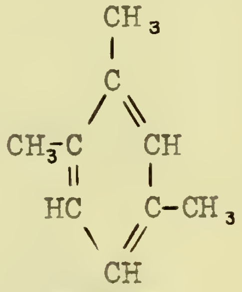
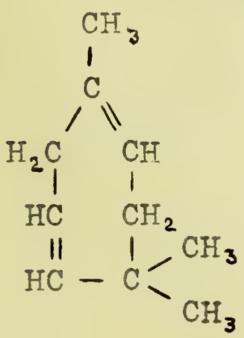
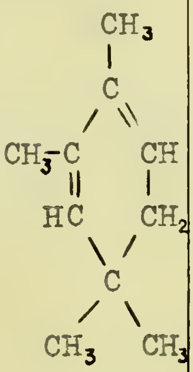
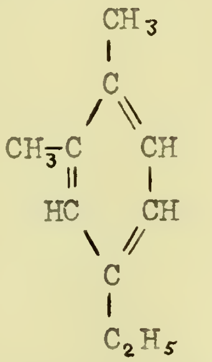
TABLE IV.

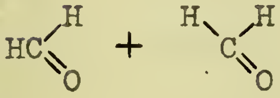
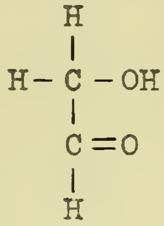
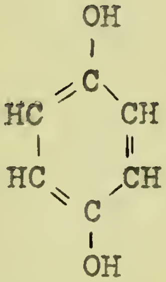
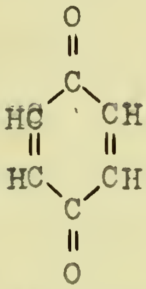
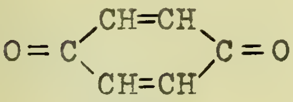
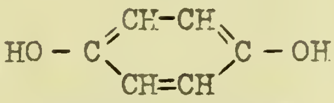
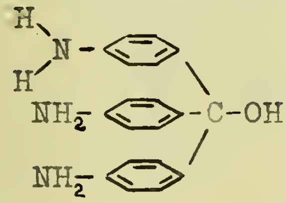
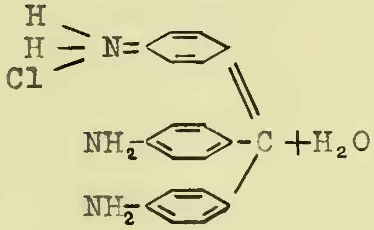
Rearrangements with Reactions According to Classes of Table II.

Class	Rearrangement		Reaction.
	Before.	After.	
I	 $CH_3-\overset{CH_3}{\underset{OH}{C}}-\overset{CH_3}{\underset{OH}{C}}-CH_3$ Pinacone	 $CH_3-\overset{CH_3}{\underset{H_3C}{C}}-\underset{\overset{\|}{O}}{C}-CH_3 + H_2O$ Pinacolene	Distilled with dil. H_2SO_4
	 $CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\underset{OH}{CH}-CH_3$ 3,3,Dimethyl-butanol (2)	 $CH_3-\overset{CH_3}{C}-\overset{CH_3}{C}-CH_3 + H_2O$ Tetramethyl ethylene.	Dehydration simultaneous with reduction of Pinacolene with HI
	 $HOOC-\overset{CH_3}{\underset{CH_3}{C}}-CH=CH-COOH + H_2$ Dimethyl glutaconic acid.	 $HOOC-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}-COOH$ Dimethyl glutonic acid.	Reduction H_2
	$(C_6H_5)_2C=C(C_6H_5)_2 + O_2$ Tetra phenyl ethylene	 $(C_6H_5)_3C-\underset{\overset{\|}{O}}{C}-C_6H_5$ Benzoyl triphenyl methane.	Oxidation O_2
	$C_6H_5CH-(OH)-CH(OH)-C_6H_5$ Hydrobenzoin	 $(C_6H_5)_2CH-\underset{H}{C}=O + H_2O$ Diphenylacetaldehyde.	Dehydration by H_2SO_4
	$C_6H_5CO-CO-C_6H_5 + H_2O$ Benzil	$(C_6H_5)_2C(OH)-COOH$ Benzilic acid.	Fusion with KOH
	$R-CH=CH-CH=CH-COOH + H_2$ Acids of Sorbic acid group.	$R-CH_2-CH=CH-CH_2-COOH$ Δ^2 Acids.	Na amal. CO_2 passed in to remove OH^- and decrease speed of reaction.

II	 Double union in shifting triphenyl	 of benzoid to quinoid in methane dyes.	Acids. H^+
	 Phenyl dimethyl Indolinol	 Dimethyl Indol.	HCl
	 Gem Dimethyl dihydro resorcinol.	 Dichlor o-oxylene.	Dehydration.
	Reduction of  $\Delta^{1,3}$ Dihydroterephthalic acid.	Unsaturated acids.  Δ^{2} Tetrahydroterephthalic acid.	Reduction.
	 $\Delta^{1,4}$ Dihydroterephthalic acid	 Δ^{2} Tetrahydroterephthalic acid.	Reduction.
	 Phthalic acid.	 Δ^{2} Tetrahydrophthalic acid.	Na amal. High T. presence OH^-

	 + NaHg Low T. Terephthalic acid.	 $\Delta^{2,5}$ Dihydroterephthalic aci	Na amal. in cold and CO_2
	 + 2HBr & -2HBr $\Delta^{1,3}$ Dihydroterephthalic acid.	 Δ^{2} Tetrahydroterephthalic acid.	Dehalogenation
	 αα' Dibrom-hexahydroterephthalic acid.	 $\Delta^{1,3}$ Dihydroterephthalic acid.	Alcoholic KOH
	 + H_2 Dihydroterephthalic acid.	 Δ^{2} Tetrahydroterephthalic acid.	Reduction in the cold.
	 + H_2 $\Delta^{1,3}$ Dihydroterephthalic acid.	 Δ^{2} Tetrahydroterephthalic acid.	" "
	 + H_2 $\Delta^{1,4}$ Dihydroterephthalic acid.	 Δ^{2} Tetrahydrophthalic acid.	Reduction.
	 + NaHg in atm. CO Benzoic acid.	 Δ^{2} Tetrahydrobenzoic acid.	Reduction Na amal. and CO_2.
	 + HBr & - HBr Δ^{2} Tetrahydrobenzoic acid.	 Δ^{1} Tetrahydrobenzoic acid.	Dehalogenation
	 + NaHg cold $\Delta^{1,3}$ Dihydrobenzoic acid.	 Δ^{2} Tetrahydrobenzoic acid.	Reduction Na amal. in cold
	 + NaHg heat $\Delta^{1,3}$ Dihydrobenzoic acid.	 Δ^{1} Tetrahydrobenzoic acid.	Reduction Na amal. Heat

III	Change of Dyes to Color Bases.		
			OH⁻
	 Isogeraniolene	 Trimethyl benzene	Bromination and subsequent dehalogenation.
	 Isogeranolene	 Pseudo cumene	" "
IV	Color Base to Dye. Triphenyl methane	series etc.	H^+
	 Euterpene 	 Ethyl-o-xylene	Bromination. Dehalogenation.

V	Polymerization - Aldol Condensation Rearrangement Between Molecules.		
			OH^- H^+
XIII	Double Union from Ring to Side Chain.		
	 Hydroquinone	 Quinone	Oxidation
	Double Union from Side Chain to Ring.		
	 Quinone	 Hydroquinone.	Reduction.
XV			Acids.

General Comment Upon Tables III and IV.

In these tables illustrations of the different types of known reversible and non-reversible rearrangements are given. It is evident that hydrogen, the double union (which in general is the same thing as the shifting of hydrogen) and the alkyl group are more easily rearranged than the other elements or radicals. Further, rearrangements occur much more frequently between nitrogen and carbon, the shifting occurring between side chain nitrogen and ring carbon. The alkyl, acyl, arcyl (aromatic acid radical), hydroxyl, amine, alkyl amine, arryl amine, nitro, nitroso, halogen and sulphonic acid radicals undergo this rearrangement, (members of class XIX).

In general, however, the oxy-alkyl and arryl and alkyl, arryl, nitro, nitroso, and haloamine groups do not rearrange as a whole, but rather the alkyl, arryl, nitro, nitroso, and halogen shift from the oxygen or nitrogen to carbon.

Comment Upon Table III.

In this table the true reversible and non-reversible rearrangements are classified, excepting the members of classes 37 to 48 inclusive and space rearrangements.

The reagents causing these rearrangements are hydrogen and hydroxyl ions, with or without heat, heat and rarely pressure. In a few cases zinc chloride is employed but its hydrolysis would produce hydrogen ions which may have caused the rearrangements.

These reagents, hydrogen and hydroxyl ions, heat and pressure, are those commonly employed to increase the speed of reactions. The full significance of this fact will be brought out in the discussion of table IV.

From the ionization constants of the isomers before and after the reaction, it is evident that true rearrangements take place in

the direction in which the free energy of ionization is decreased, that is, in the direction to increase stability.

Comment Upon Table IV.

In this table the rearrangements occurring simultaneously with other reactions, are classified excepting those of classes 37 to 48 inclusive and space rearrangements.

It is much more difficult to determine the exact reagents which cause this class of rearrangements since so many different factors enter into the reactions. For this reason it is important to consider carefully the kind of reactions associated with rearrangements. In general such reactions are oxidation, reduction, dehydration and dehalogenation. These reactions may be said to cause the rearrangements indirectly.

The study of this type of rearrangement furnishes the support for the principle that rearrangements are due to the catalytic influence of the hydrogen and hydroxyl ions, heat and pressure upon the speed of reaction with which the compound is changing into a more stable isomer. At ordinary temperature in the absence of these catalyzers the same reaction is taking place but at such a slow rate that it may escape detection. This conception is common to organic chemists, especially in the case of the saponification of esters which proceeds slowly at ordinary temperature in the presence of water, but at a much greater rate in the presence of hydroxyl or hydrogen ions. Further the rate of saponification is proportional to the concentration of these ions which should also be the case with rearrangements. This point will be studied later.

Baeyer in his work upon the phthalic acids has furnished the necessary experimental proof of the catalytic action of temperature

and ions upon rearrangements. Terephthalic acid gives $\Delta^{2,5}$ dihydroterephthalic acid upon reduction with sodium amalgam in the cold, while carbon dioxide is passed thru the solution to remove the hydroxyl ions. This acid gives the $\Delta^{1,5}$ isomer when warmed with water and the latter gives the $\Delta^{1,4}$ acid in the presence of hydroxyl ions. From the curves accompanying table V. and the discussion of the same, it will be seen that the $\Delta^{1,4}$ dihydroterephthalic acid is the most stable of the three isomers, while the $\Delta^{2,5}$ acid is the most unstable. Hence the rearrangements took place in the direction to produce more stable compounds as Baeyer stated from a study of their chemical properties. Temperature catalyzed the rate of change of the $\Delta^{2,5}$ acid into the $\Delta^{1,5}$ isomer, while hydroxyl ions catalyzed the rate of change of the $\Delta^{1,5}$ acid into the stable $\Delta^{1,4}$ isomer. Baeyer noted that, at higher temperatures and in the presence of hydroxyl ions, the unstable $\Delta^{2,5}$ acid was not formed but a more stable product resulted. This supports Nernst's statement that the existance of more than one form in each series is dependent upon the smallness of the reaction velocity at the time of formation.

Similarly, the reduction of phthalic acid by sodium amalgam at high temperature, in the absence of carbon dioxide gas should give a very stable hydrogenated acid. Baeyer found that these conditions gave a Δ^{2} tetrahydrophthalic acid. Reference to table V. will show that this acid is the most stable of any of the dihydro- or tetrahydro- acids. Again, it is seen that the speed of reaction was so great that the unstable intermediate dihydro- acids could not exist and again the above principle is supported.

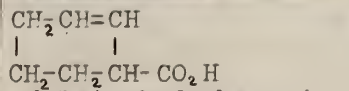
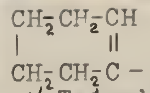
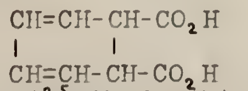
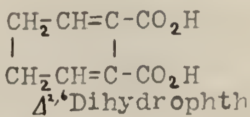
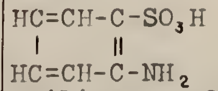
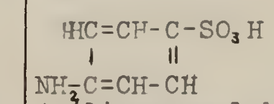
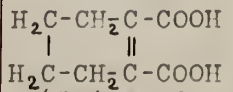
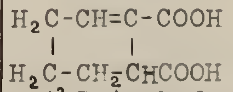
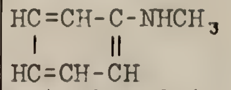
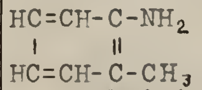
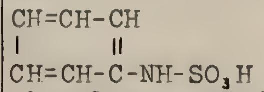
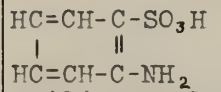
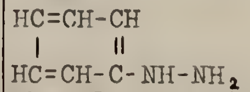
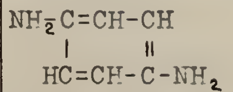
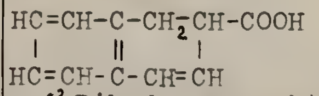
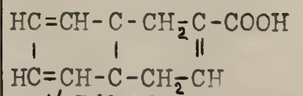
A study of table IV. and its reactions in the light of the above remarks throws some light upon the principle underlying

Thiele's partial valence theory. The products obtained by the reduction of $\Delta^{1,3}$ unsaturated acids appears to be the unstable Δ^{2} unsaturated acids. From the above it is evident that such reductions must be carried out under conditions where the speed of reaction is small or else more stable products would result.

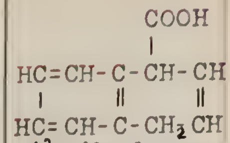
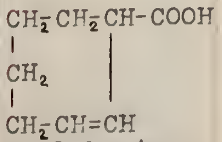
x 10^{10}

TABLE V.

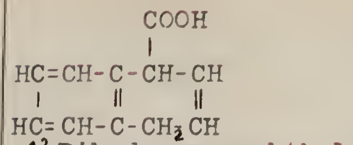
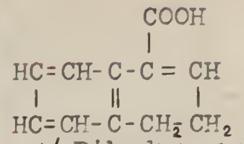
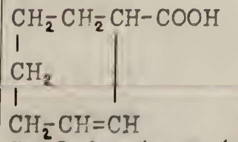
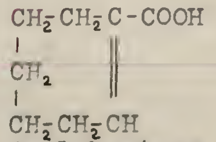
Energy Relation of True Rearrangements.

Class	True Rearrangements.		Catalyzer	Ionization Constants.			
	Before.	After.		Before. K x 10.	After. K x 10.	Before. Log. K x 10^{10}	After. Log. K x 10^{10}
I	$CH_3CH_2CH=CH$-CH_2CO_2H * Dihydrosorbic acid.	$CH_3CH_2CH_2CH=CH$-CO_2H * Δ' Hexenic acid.	OH^-	2.64 -5	1.89 -5	5.423	5.2775
II	 $CH_2CH=CH$ * | | CH_2-CH_2CH-CO_2H Δ^2 Tetrahydrobenzoic acid.	 CH_2CH_2CH * | ‖ CH_2CH_2C - CO_2H Δ' Tetrahydrobenzoic acid.	OH^-	3.05 -5	2.21 -5	5.478	5.344
	 CH=CH-CH-CO_2H * | | CH=CH-CH-CO_2H $\Delta^{2,5}$Dihydrophthalic acid.	 $CH_2CH=C$-CO_2H * | | $CH_2CH=C$-CO_2H $\Delta^{1,4}$Dihydrophthalic acid.	OH^-	2.46 -4	1.65 -4	6.392	6.218
	 HC=CH-C-SO_3H | ‖ HC=CH-C-NH_2 Aniline-o-sulphonic acid.	 HC=CH-C-SO_3H | ‖ NH_2-C=CH-CH Aniline-p-sulphonic acid. (Sulphanilic acid).	Heat H_2SO_4	3.3 -3	5.81 -4	7.519	6.764
	 H_2C-CH_2-C-COOH | ‖ H_2C-CH_2-C-COOH Δ' Tetrahydrophthalic acid	 H_2C-CH=C-COOH | | H_2C-CH_2-CHCOOH Δ^2 Tetrahydrophthalic acid	OH^-	5.9 -4	7.6 -5	6.772	5.882
XVI & XIX	 HC=CH-C-$NHCH_3$ | ‖ HC=CH-CH Methyl anilin	 HC=CH-C-NH_2 | ‖ HC=CH-C-CH_3 Toluidine.	Heat	K_b^{60} 7.4 -9	K_b^{60} 1.09 -9	1.869	1.038
XIX	 CH=CH-CH | ‖ CH=CH-C-NH-SO_3H Phenyl sulphamic acid.	 HC=CH-C-SO_3H | ‖ HC=CH-C-NH_2 Anilin-o-sulphonic acid.	H^+	1. -1	3.3 -3		
	 HC=CH-CH | ‖ HC=CH-C-NH-NH_2 Phenyl hydrazine	 NH_2-C=CH-CH | ‖ HC=CH-C-NH_2 p-Phenylene diamine.	Heat HCl $(H)^+$	K_b^{40} 1.6 -9	K_b^{25} 3.1 -10	1.204	0.492
(1)	 HC=CH-C-CH_2-CH-COOH * | ‖ | HC=CH-C-CH=CH Δ^2 Dihydro-B-naphthylic acid.	 HC=CH-C-CH_2-C-COOH * | | ‖ HC=CH-C-CH_2-CH Δ' Dihydro-B-naphthylic acid.	OH	5.9 -5	2.9 -5	5.772	5.463

1. See class II.

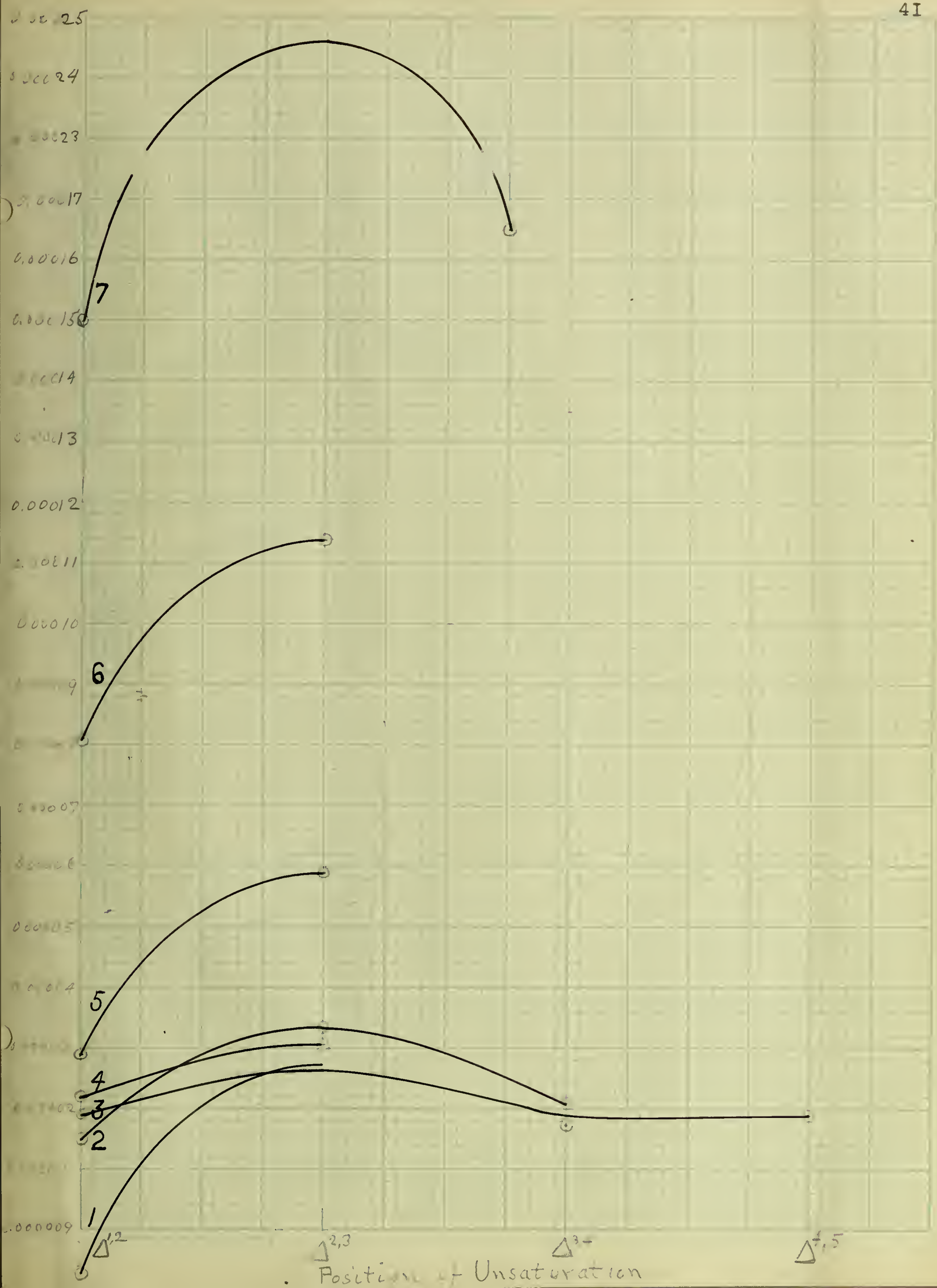
	 Δ^2 Dihydro-α- acid.	6.058	5.909
	 Cycloheptene ylic acid.	5.433	4.919
(1)	$CH_3CH=CH-CH_2C$ Δ^2 Pentenic	5.526	5.172

1. See class I.

	 * Δ^2 Dihydro-α-naphthylic acid.	 * Δ' Dihydro-α-naphthylic acid.	OH	1.14 -4	8.1 -5	6.058	5.909
	 * Cycloheptene (2) Carboxylic acid.	 * Cycloheptene (1) Carboxylic acid.	OH	2.7 -5	8.3 -6	5.433	4.919
(1)	$CH_3CH=CH-CH_2COOH$ * Δ^2 Pentenic acid.	$CH_3CH_2CH=CH-COOH$ * Δ' Pentenic acid.	OH	3.35 -5	1.48 -5	5.526	5.172

1. See class I.

Curves I


0.00025
0.00024
0.00023
0.00017
0.00016
0.00015
0.00014
0.00013
0.00012
0.00011
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0.00009
0.00008
0.00007
0.00006
0.00005
0.00004
0.00003
0.00002
0.00001
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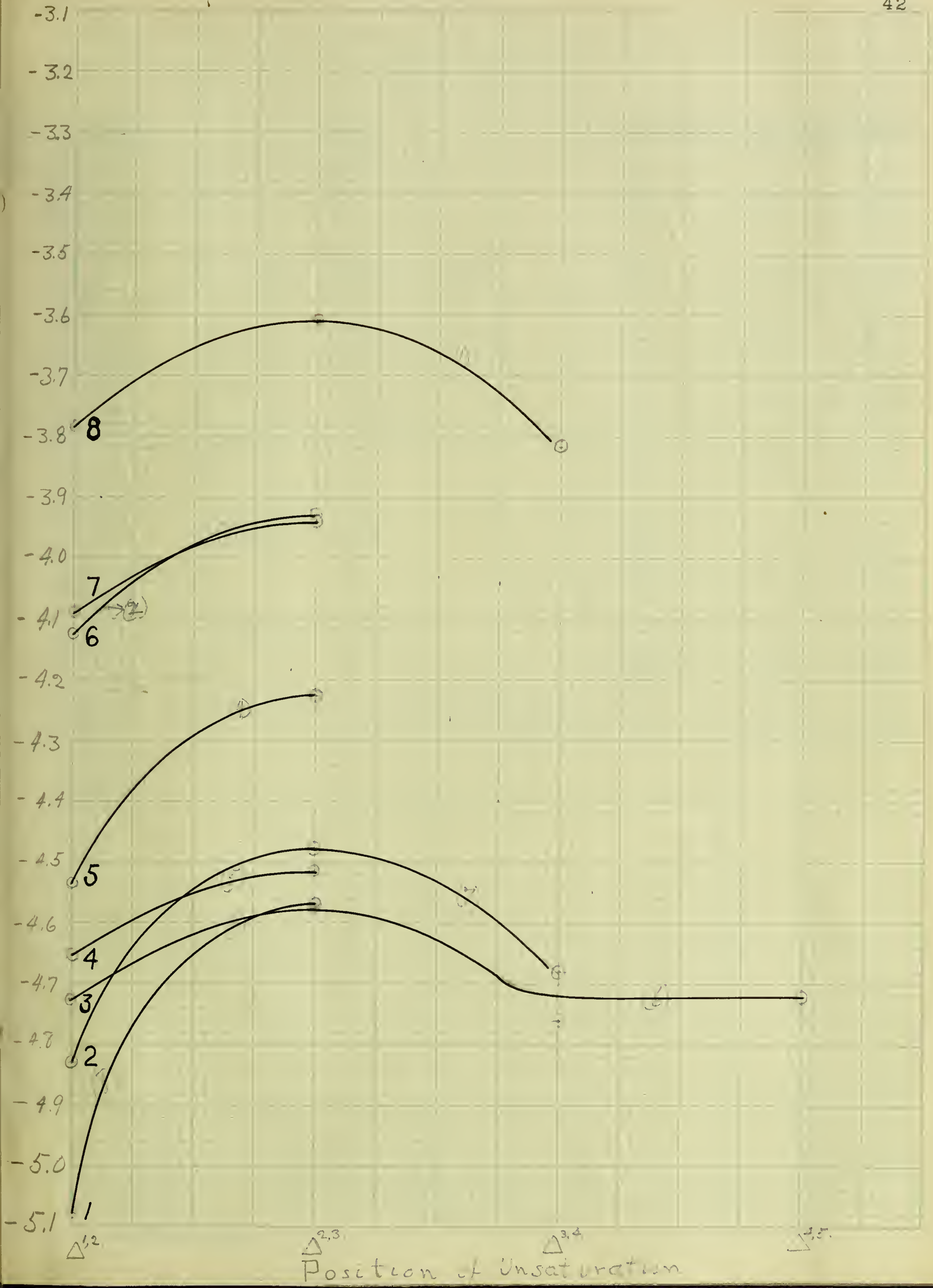
7
6
5
4
3
6
2
1
Δ1,2
Δ2,3
Δ3,4
Δ4,5
Position of Unsaturation

Curves I


-3.1
-3.2
-3.3
-3.4
-3.5
-3.6
-3.7
-3.8
-3.9
-4.0
-4.1
-4.2
-4.3
-4.4
-4.5
-4.6
-4.7
-4.8
-4.9
-5.0
-5.1
8
7
6
5
4
3
2
1
Δ1,2
Δ2,3
Δ3,4
Δ4,5
Position of Unsaturation

Data for Curves I.

Curve number.	Name.	Ionization Constant.		
		K x 10.	Brigg's Log.	
1.	$\Delta^{2,6}$Dihydrophthalic acid	1.65 -4	4.218	-3.782
	$\Delta^{2,5}$ " " "	2.46 -4	4.392	-3.608
	$\Delta^{2,4}$ " " "	1.5 -4	4.177	-3.823
2.	Δ^{2}Tetrahydrophthalic acid.	7.5 -5	5.876	-4.124
	Δ^{1} " " "	1.18 -4	4.0725	-3.9275
3.	Δ^{1}Dihydro α naphthylic acid.	8.1 -5	5.909	-4.091
	Δ^{2} " " " "	1.14 -4	4.058	-3.942
4.	Δ^{1} Dihydro β naphthylic acid.	2.9 -5	5.463	-4.537
	Δ^{2} " " " "	5.1 -5	5.772	-4.228
5.	Δ^{1} Tetrahydrobenzoic acid	2.21 -5	5.345	-4.655
	Δ^{2} " " "	3.05 -5	5.485	-4.515
6.	Δ^{1} Hexenic acid.	1.89 -5	5.277	-4.723
	Δ^{2} " "	2.64 -5	5.423	-4.577
	Δ^{3} " "	1.74 -5	5.241	-4.759
	Δ^{4} " "	1.91 -5	5.282	-4.718
7.	Δ^{1} Pentenic acid.	1.48 -5	5.172	-4.828
	Δ^{2} " " "	3.35 -5	5.526	-4.474
	Δ^{3} " " "	2.09 -5	5.322	-4.678
8.	Cycloheptene (1) Carboxyllic (1)	8.3 -6	6.919	-5.081
	" " (2) " " (1)	2.7 -5	5.432	-4.568

Comment upon Table V. and Curves I.

In the discussion of chemical stability, the reasons for using the free energy of ionization as a measure of stability were given and the free energy of ionization was found to be proportional to the logarithm of the affinity constant .

Table V. and the accompanying curves furnish the experimental data for some of the acids and bases that undergo molecular rearrangement. Since the stability of the rearranging compound is inversely proportional to the logarithm of the ionization constant, the compound before rearranging should have a larger affinity constant than the resulting isomer. This is found to be the case with all true rearrangements where the data are available. The ionization constant was determined at 25° in water solution unless otherwise specified, the values being taken from "Affinitat messungen an schwachen Säuren und Basen" von Harold Lundén. In the cases where the rearrangement does not occur at this temperature, it would be more accurate to determine the affinity constant at the temperature of the reaction or to extrapolate the same, but since only a qualitative measure of the free energy of ionization is necessary at this time the above corrections have not been applied.

From table V., it is evident that the statement made by Fichter and Pfister [1] that the Δ^2 unsaturated acid gives an affinity constant greater than any of its isomers is generally true. This principle holds for ring acids as well as for open chain acids where it was first observed. The curves accompanying table V. show this principle graphically. The first set of curves is plotted from the algebraic values of the affinity constants starred in table V.

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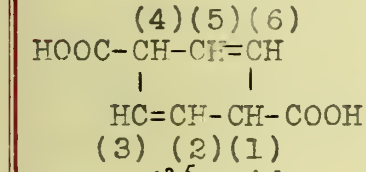
1. Fichter and Pfister. Annalen 334 (1904),203.

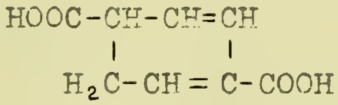
The second set of curves is plotted from the Brigg's logarithm of the same affinity constants since it is the logarithmic function of the affinity constant that is proportional to the free energy of ionization as given by the expression $A = R\ T\ \ln K$. The curves show clearly the general principle that of all its isomers, the Δ^2 unsaturated acid exhibits the most free energy of ionization and is therefore the most unstable of all the isomers. If, as is the case with ring acids, there are two double unions in the molecules, then the acid having both double unions in the Δ^2 position with respect to the carboxyl groups, has the greatest ionization constant of all isomeric forms, that is, exhibits the greatest amount of free energy of ionization and is the most unstable. The proof of these stataments is given by the above tables and curves. Hence it becomes evident that one may safely argue that a Δ^2 unsaturated acid is the most unstable of all its isomers without determining the ionization constant and the principle may be considered absolutely general.

In the discussion of table.IV., Baeyer drew certain conclusions concerning the stability of certain ring acids because of their chemical behavior. The writer stated that he was correct and that a measure of their free energy was in accordance with this view. Terephthalic acid when reduced by sodium amalgam in the cold and in the presence of carbon dioxide gas, gave $\Delta^{2,5}$ dihydroterephthalic acid, the most unstable of all the dihydro- acids. This product warmed with water gave the $\Delta^{1,5}$ acid by rearrangement while the latter gave the $\Delta^{1,4}$ acid by a second rearrangement catalyzed by the hydroxyl ion. According to the principle that true rearrangements must proceed in the direction to decrease their free energy, the ionization constant of the $\Delta^{2,5}$ dihydroterephthalic acid must be greater than

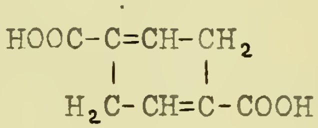
that of the $\Delta^{1,5}$ acid and the latter greater than that of the $\Delta^{1,4}$ acid. The $\Delta^{2,5}$ acid contains two double unions in the Δ^{2} position to carboxyl groups, the $\Delta^{1,5}$ acid one double union in the Δ^{2} position to a carboxyl group, and the $\Delta^{1,4}$ acid contains no double union in the Δ^{2} position to either carboxyl group. Further the generality of the principle just established by the curves makes the measurement of these constants unnecessary and their stability follows from the position of the double unions which the following formulae will show:



$\Delta^{2,5}$ acid.



$\Delta^{1,5}$ acid.



$\Delta^{1,4}$ acid.

Thus the stability relations of the dihydroterephthalic acids in terms of free energy is established as was necessary to prove the catalytic influence of the hydrogen and hydroxyl ions, temperature, and pressure upon speed of reaction with which these acids are changing into each other as well as the reason for the direction in which the rearrangements proceeded.

Cause of Molecular Rearrangements.

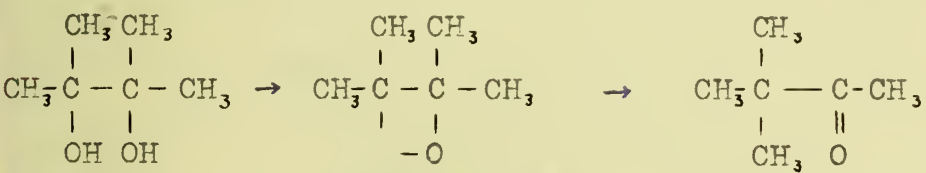
It is a fundamental principle of thermodynamics that the free energy of the universe tends toward a minimum. All reactions occur in this direction when all of the reacting substances in the reaction are considered. The diminution of the free energy of a reaction is, therefore, the driving principle of every chemical reaction. The operation by which this decrease of free energy is accomplished must be considered simply a machine by means of which the free energy is decreased.

In the case of true rearrangements, this diminution of free energy is readily traced out, since the only reaction is the rearrangement, and the only reacting substance is the one rearranging. The rearrangement proceeds slowly in the absence of the catalyzer, but in its presence the rate of change is greatly accelerated. Hence the catalytic material is simply a machine by which the same end is accomplished more quickly.

Rearrangements occurring simultaneously with other reactions present a more complicated case. The diminution of free energy is concerned with several different reactions. For example, the reduction of terephthalic acid under the conditions above described gave $\Delta^{2,5}$ dihydroterephthalic acid, which possesses less free energy of ionization than terephthalic acid. Yet the most unstable of all, the dihydroterephthalic is produced. It has been shown that such reactions result under conditions where the speed of formation, is reduced to a minimum, and where the diminution of free energy of reaction is a minimum. Thus it is apparent that the cause of such rearrangements is due to the imperfect machine used to accomplish the change. The slow speed of reaction forces the change

to take place so that the decrease in free energy of ionization is a minimum. The rearrangement is simply the structural picture of the molecule adjusting itself so as to suffer a minimum decrease in the free energy. As Baeyer showed, if the same reaction is carried out so that the speed of reaction is greatly increased, then the diminution in the free energy of ionization is also greatly increased and the most stable tetrahydroterephthalic acid is produced.

Table IV contains many illustrations of another type of rearrangement , in which the law of constant valence for the carbon atom in organic compounds appears to be the driving force. The historic illustration of this class is that of the pinacone-pinacolene rearrangements:



$$CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{OH}{\overset{CH_3}{C}}-CH_3 \rightarrow CH_3-\underset{|}{\overset{CH_3}{C}}-\underset{-O}{\overset{CH_3}{C}}-CH_3 \rightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{\overset{\Vert}{O}}{C}-CH_3$$

Pinacone Intermediate Pinacolene.

The cause of this rearrangement may also be attributed to the inability of the free radical (intermediate product) to exist. Every attempt to isolate a free radical has resulted in the union of the free radicals with themselves as illustrated by the Würtz and Fittig syntheses. One possible exception to this statement may be the case of triphenyl methyl discovered by Gomberg, who thinks the free radical occurs in solution. If Gomberg is correct, then the reactivity of his product suggests the great amount of free energy that must be associated with a free radical and that rearrangements would occur with great velocity to diminish the same. Thus again the structural

formula gives a picture of the readjustment of energy within the molecule so that the free energy of reaction may be decreased. It is also apparent that an energy consideration underlies the law of constant valence of elements in organic compounds.

PART II

CONSTITUTION OF LAUROLENE

HISTORICAL

1872 — 1909

Laurolene was first obtained by Felix Wreden[1] who was studying the behavior of oxycamphoric acid anhydride (camphanic acid). He noted that dry distillation of the potassium salt of, as well as the action of hydriodic acid at 150° . upon, the oxycamphoric acid anhydride gave a hydrocarbon, C_8H_{14} , which possessed the boiling point of 119° and specific gravity at 0° . equal to 0.814. Further he decided that the hydrocarbon was optically inactive and that exposure to the oxygen of the air yielded a brown oxidation mass, from which he concluded the hydrocarbon was unsaturated. He next attempted to prepare its saturated reduction product by the action of hydriodic acid upon camphanic acid at high temperatures, but obtained only laurolene. By a similar action of hydriodic acid upon camphoric acid at 200° , he had obtained tetrahydrometaxylene and hence he concluded that the product from camphanic acid (oxycamphoric acid anhydride) was also a xylene derivative.

Reyher [2] obtained laurolene by heating barium camphanate with water at high temperatures. From Wreden's observations it is evident that he obtained laurolene 19 years earlier by this same method, though he apparently did not recognize it for he stated that the barium and silver salts of oxycamphoric acid anhydride (camphanic acid) when boiled with water yield a very volatile oil. By application of this method Reyher showed the product resulting was laurolene.

Hans Rupe and Carl Maull [3] repeated Wreden's work and showed that heating camphanic acid alone with water gave no laurolene.

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[1] Felix Wreden - Ann.I63, 336 (I872).

[2] Reyher - Inaug. Dissert. Leipzig 1891 - 51 (see Ann. 290, I85 (I896).

[3] Hans Rupe & Carl Maull - Ber. 25, 92I (I893).

But by distillation of its potassium salt, as Wreden stated, laurolene was obtained, which he showed was very different from the isomer C_8H_{14}, which Wreden obtained by heating camphoric acid with hydriodic acid to 200°. This latter product was thoroughly studied by Wallach [1].

Attention was again called to laurolene by Ossian Aschan [2], who found that the slow distillation of camphanic acid in a current of carbon dioxide gas gave a hydrocarbon which, from its association with lauronolic acid, he named laurolene. In the paper [3] which gives the results of several years work upon laurolene, Aschan showed that Fittig and Woringer [4] had overlooked this product inthe distillation from camphanic acid at high temperature. Besides lauronolic acid and campho-lactone, Aschan obtained a very volatile oil, boiling at 120° and possessing the characteristic terpentine or camphor-like odor. Analysis showed this product to be the hydrocarbon, laurolene, C_8H_{14}. The density, $d_{4°}^{18.6°}=0.080187$ also showed it to be identical with the product Wreden obtained from oxycamphoric acid anhydride (camphanic acid). But differing with Wreden he found it to be optically active, $(\alpha)_j=-23.0°$. He further found, as did Reyher, that it was unsaturated as shown by its reduction of potassium permanganate solution and its addition of bromine. At 18° he found its molecular refraction to be 36.7, while that calculated for a cyclic compound containing one ethylene union was 36.43. Hence, Aschan concluded that laurolene was a cyclic compound con-

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[1] Wallach Ber. 25, 92I (I892).
[2] Ossian Aschan Ber. 27, 3507 (I894).
[3] Ossian Aschan Ann. 290, I85 (I896).
[4] Fittig & Woringer Ann. 227, I.

taining one double union. Since Wreden had isolated from camphoric acid a tetrahydrometaxylene as subsequently proven by making the trinitrometaxylene, Aschan concluded laurolene might be a cyclohexene compound. But nitration with a mixture of sulphuric acid and nitric acid under varying conditions gave only a tar. Baeyer [1] has shown that potassium ferricyanide would remove hydrogen from a partially hydrated aromatic compound regenerating the aromatic substance. Accordingly Aschan applied the method to laurolene but no aromatic hydrocarbon resulted. Hence he concluded that laurolene did not contain a six carbon ring. The action of potassium permanganate upon laurolene gave him only acetic, oxalic and a small amount of other lower fatty acids. Applying this same method of oxidation the writer succeeded in establishing the constitution of laurolene and it is evident that Aschan lost the main oxidation product by filtering off the manganese dioxide before extraction with ether.

While Aschan was carrying on the above described work, W. A. Noyes [2] prepared laurolene by the action of sodium nitrite upon the hydrochloride of aminolauronic acid at ordinary temperature. The product possessed the boiling point 122° . and the density $d^{15°}_{15°} = 0.8033$ and $d^{20°}_{20°} = 0.8004$, while the yield was 6 per cent. by weight of the chloride used. The hydrocarbon analyzed for the formula C_8H_{14}. When four atoms of bromine were cautiously added to it and the mixture heated in a sealed tube to 200°, the charring was characteristic of pentamethylene compounds as discovered by Perkins [3]. This observation is of peculiar interest since laurolene actually possesses such a structure.

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1 Baeyer - "Gesammte Werke".
2 W.A.Noyes - Am. Chem. J. 17, 432. Ber.28, 553 (I895).
3 Perkins - J. Chem. Soc. 51, 247. 65, 979.

Simultaneously, J. Walker and J. Henderson[1] obtained a hydrocarbon by the distillation of allocampholytic acid obtained from the electrolysis of the potassium salt of alloethylic camphorate. It possessed the boiling point 120°, and the optical rotation $(\alpha) = -29.2°$, hence the product was laurolene.

Noyes' method for the preparation of laurolene was confirmed by the work of Tiemann [2]. He found the hydrocarbon to boil at 121 - 122° and to possess the density 0.8008 at 17.5 , while its optical activity gave $(\alpha)_D = 19.9°$.

Zelinsky and Lepeschkin [3] were the next to investigate laurolene. By the action of hydriodic acid upon laurolene, prepared by Aschan's method, at high temperatures they succedded in preparing an iodide derivative distilling at 69° under 15 m.m. pressure. This product, upon reduction by means of a zinc palladium method at the temperature of the water bath,,gave a saturated hydrocarbon boiling at 114-115° whose density determinations gave $d^{19°}_{4°} = 0.7688$. It was found to be optically inactive and gave on analyses the formula C_8H_{16} , so they considered it dihydrolaurolene. Similar action upon isolaurolene gave a dihydroisolaurolene which they concluded was identical with dihydrolaurolene. Believing this reduction product to be a cyclohexane derivative, therefore a hexahydroxylene, they prepared synthetically the ortho, meta and paraxylenes and found them to possess boiling points higher than that of dihydrolaurolene (or dihydroisolaurolene). Since its density placed it among the cyclohexane derivatives, it must have the remaining pos-

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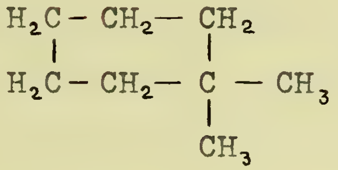
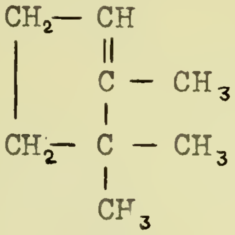
1 Walker & Henderson J. Chem Soc., <u>69</u>, 758 (1896).
2 Tiemann - Ber. 33, 2935.
3 Zelinsky & Lepeschkin - Ann. 319, 303 (1901).

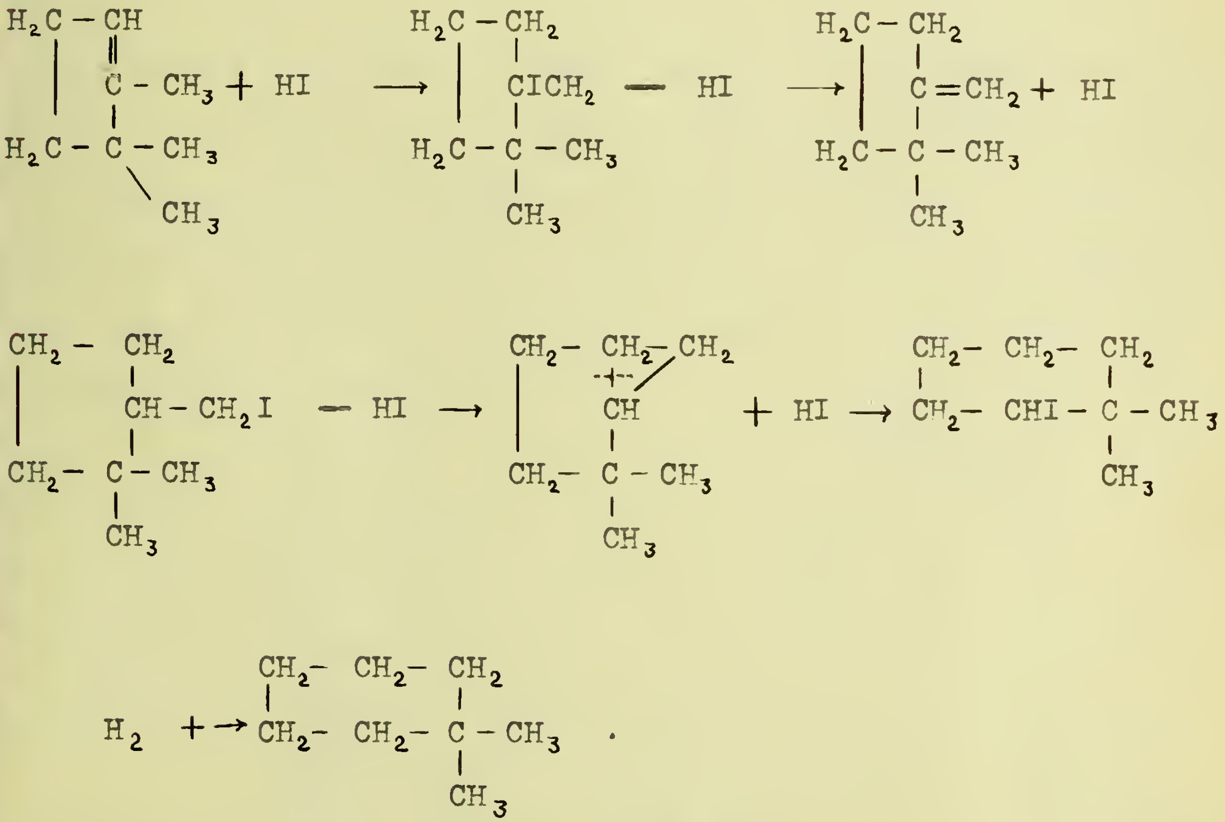
sibility for a dimethylhexahydroxylene namely the gem-dimethylhexahydroxylene,



Blanc's work upon isolaurolene had definitely proven that it possessed the structure

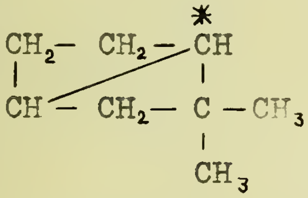


and was therefore a cyclopentene derivative. To explain the structure of dihydroisolaurolene, a cyclohexane derivative, Zelinsky made use of the following rearrangements:

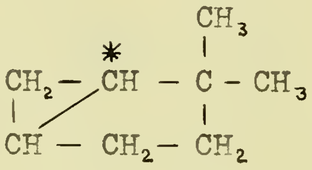


The cause of the rearrangement above was attributed to the prolonged

heating at 200° necessary to form the iodide. But by the elimination of hydriodic acid from the iodide by means of dimethyl aniline, the original isolaurolene was regenerated and Zelinsky found much difficulty in seeing how the above rearrangements could be reversed. As a result he concluded that the constitution of isolaurolene given by Blanc was incorrect and stated that isolaurolene and laurolene possessed the following constitutions:



Isolaurolene.



Laurolene.

This, then, was the first attempt to assign a structure to laurolene. How daring this attempt was may be gathered from the following article.

Crossley and Renouf [1] were unwilling to accept the above constitution for laurolene so that the work of Zelinsky and Lepeschin was repeated. They prepared laurolene from camphanic acid by distillation as did Zelinsky and Lepeschin and like them found the following values for the rotation and density of the fraction which boiled at 119.5 - 120.5° .

Density.	Rotation.
$d_{4^\circ}^{4^\circ} = 0.8097$	(1) $(\alpha)_D = 11.4^\circ$
$d_{10}^{10^\circ} = 0.8048$	(2) Inactive.
$d_{15}^{15^\circ} = 0.8010$	(3) $(\alpha)_D = 6.6^\circ$
$d_{20}^{20^\circ} = 0.7974$	(4) $(\alpha)_D = 6.6^\circ$
$d_{25}^{25^\circ} = 0.7939$	(5) $(\alpha)_D = 4.1^\circ$

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[1] Crossley & Renouf - J. Chem. Soc., 87, 1487; 89, 26.

So like Zelinsky they concluded that laurolene was a mixture of isomers. Its iodide was next prepared and upon reduction gave dihydrolaurolene, possessing the same physical constants as stated by Zelinsky and Lepeschkin. The same changes were carried out with isolaurolene and the dihydroisolaurolene upon oxidation gave α,α dimethylglutaric acid. Oxidation of dihydrolaurolene, however, gave a small quantity of a syrup and oxalic acid but no glutaric acid. Hence Crossley and Renouf had proven that dihydrolaurolene and dihydroisolaurolene were not identical as stated by Zelinsky and Lepeschkin. Furthermore, the gem-dimethylhexahydrobenzene was made synthetically and found to have the following constants when compared to dihydrolaurolene (or dihydroisolaurolene).

	Gem-dimethylhexahydrobenzene	Dihydrolaurolene.
Boiling point	120°	111.5-114°
Spec. Grav.	0.7864	0.7633
Odor	Like geranium	Camphoraceous
Oxidation Product	Dimethyl adipic acid	Oxalic acid

Hence not only were the two isomeric hydro compounds different in structure, but neither was the gem-dimethylhexahydrobenzene. Thus the structure of laurolene still remained unknown, so Crossley and Renouf attempted to determine the same by the action upon laurolene of bromine, nitrosyl chloride, nitrating mixtures, nitric acid and finally permanganate, but with the same results as the earlier investigators found.

W. A. Noyes and Rene de M. Taveau [1] obtained laurolene by the action of an alcoholic solution of sodium hydroxide upon the nitroso

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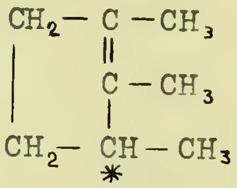
[1] Noyes and Rene de M. Taveau. Am. Chem. J. 32, 285 (1904), 35, 380 (1906).

derivative of the anhydride of aminolauronic acid. Since this method gave trouble from intermediate products it was further perfected by using an aqueous solution of alkali to decompose the nitroso compound. This method gave laurolene to the extent of 27.8 per cent. by weight of the nitroso compound decomposed, while the direct action of sodium nitrite upon the hydrochloride of aminolauronic acid gave only 6 per cent. by weight.

J. F. Eykman [1] attacked the problem of the constitution of laurolene from an entirely different view point. From his refractometric studies he ascertained the connection between ring structure and molecular refraction and applying his results to laurolene assigned to it the structure,



but offered no chemical proof of the same.

Hence laurolene was finally given the structure of a cyclo pentene derivative, which will be shown to be correct by the following work.

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[1] J. F. Eykman - Chemisch Weekblad - 1907 - No. 4.

EXPERIMENTAL

1907 — 1910

LEVO-LAUROLENE.

Preparation of Levo-Laurolene.

Levo-Laurolene was prepared by the method of Noyes and Taveau [1] by boiling the nitroso derivative of the anhydride of amino lauronic acid with a 10 per cent. sodium hydroxide solution until the layer of hydrocarbon was colorless. The hydrocarbon was distilled from the solution by water vapor and after separation from the water layer, dried over fused sodium sulphate, since calcium chloride appeared to cause its polymerization. The dried product was then carefully fractionated using a micro-burner. The yield of the steam distilled hydrocarbon, after drying, gave an average yield of 29 per cent. by weight of the nitroso compound taken or 50 per cent. of the theory. A maximum yield of 53 per cent. of the theory was obtained in one experiment. The constant boiling fraction 119.6 - 120.6° gave a yield of 44.5 per cent. of the theory.

Physical Constants of Levo-Laurolene.

The laurolene, as above prepared, gave the boiling point of 120 - 122° under 750 m.m. pressure. By careful fractionation the main product could be distilled from 119.6-120.6° under 740 m.m. pressure, which fraction upon analysis gave

Calculated for C_8H_{14} : C, 87.27 ; H, 12.72.

Found C, 87.14 ; H, 12.77

Thus it is evident that the product possesses a homogeneous composition.

The hydrocarbon prepared by this method was always levo-rotary. The determination of the optical activity of a preparation which

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[1] W.A.Noyes and Rene de M. Taveau. Am. Chem. J. 35, 380 (1906).

had stood over a year, but was freshly distilled, gave $(\alpha)^{20°}_{D} = -14.5°$, while a freshly prepared sample gave $(\alpha)^{35°}_{D} = -14.7°$. When less care was taken to duplicate exactly the above proceedure for the preparation of levo-laurolene, the determination of the optical activity gave $(\alpha)^{29°}_{D} = -15.72°$ and $(\alpha)^{27°}_{D} = -18.13°$. Hence it becomes evident that levo-laurolene does not suffer mutarotation upon standing and that it is a mixture of optical or possibly structural isomers.

Reduction of Levo-Laurolene.

Many attempts were made to obtain the dihydrolaurolene. The method used was to dissolve the hydrocarbon in alcohol, add zinc dust and then pass dry hydriodic acid gas through the solution. Only negative results were obtained and the levo-laurolene was recovered unchanged. The results agreed with those of Aschan and Zelinsky. No attempts were made to effect the reduction at higher temperature since the probability of rearrangements occurring was too great and since Crossley and Renouf showed that the dihydrolaurolene gave no evidence as to the structure of laurolene.

Oxidation of Levo-Laurolene.

The hydrocarbon was oxidized with a dilute solution of potassium permanganate by a method very similar to that employed by Aschan [1]. In several oxidations acetic and oxalic acids were the only results. In the majority of cases, however, an oil having a camphoraceous odor was obtained in very small quantities. With sodium hypobromite this oil gave the test for an acetyl group and the conclusion was

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[1] Aschan - Annalen 290, I85 (I896).

that a keto acid was formed, but all attempts to isolate it pure gave negative results. In one case a product, titrating for glutaric acid, was obtained in a very small amount. It gave the correct analysis, but the quantity was too small to obtain further evidence as to its strudture. Further, all attempts to isolate it again in quantity failed.

In one of these unsuccessful experiments, the manganese dioxide was allowed to settle when a slight oily appearance was noted on the surface of the water. Accordingly, the manganese dioxide was dissolved by the addition of a solution of sodium hydrogen sulphite cautiously so as to avoid an excess. The oily appearance was still noted upon the surface of the solution which was extracted with ether. The ether, after drying over fused sodium sulphate, was distilled. Two grams of oil were thus obtained from 5 grams of the hydrocarbon oxidized. A drop of this oil added to a clear solution of phenyl hydrazine in dilute acetic acid gave the characteristic turbidity of an aldehyde or ketone group, while a test with fuchsine aldehyde reagent showed no aldehyde group present. The oil was inactive to sodium carbonate solution, hence it was a ketone.

The water residue, from which the ketone was extracted, was acidified with a dilute solution of sulfuric acid and again extracted with ether. The weight of the dried product was 2 grams. It reacted vigorously with dilute sodium carbonate solution showing its acid nature.

The two products, thus obtained, were mixed and an excess of dilute sodium carbonate added, after which the solution was extracted with ether. The product recovered from the ether (2.4 gr.)

was distilled in vacuo, the main portion coming over at 120 - 130° under 36 m.m. pressure. This product was then fractionally distilled with steam under diminished pressure. The first fractions contained the unchanged laurolene. The later fractions were extracted with ether and the dried product gave on analysis:

Calculated for $C_8H_{14}O_2$;	C, 67.60 ;	H, 9.68
Found	C, 70.48, 71.43, 62.30;	H, 10.41, 10.54, 9.86.
Calculated for $C_8H_{12}O$;	C, 77.42 ;	H, 12.90

The high analyses for a diketone were attributed to the presence of a condensed unsaturated monocyclicketone. The specific gravity determinations gave $d_4^{15°} = 0.9561$.

The analysis indicated a diketone while the specific gravity showed it to be an open chain diketone.

The part of the oxidation product soluble in sodium carbonate solution was extracted with ether, after acidifying with dilute sulfuric acid and the dried product distilled in vacuo giving mainly acetic and oxalic acids. Before distillation a trace of a keto acid was shown to be present, but distillation appeared to have decomposed it.

Other oxidations by the same method were carried out and attempts were made to obtain crystalline derivatives of both the diketone and the keto acid with negative results.

Preparation of the Diketone from Levo-Laurolene.

After many oxidations of laurolene the following method for the preparation of the diketone was found to give the most satisfactory results: Five grams of the hydrocarbon (levorotary from aminolauronic anhydride) were mixed with 50 grams of ice and 200 cc.

of a 2 per cent. solution of potassium permanganate (10 per cent. excess) were dropped in slowly while the mixture was shaken and cooled with ice water. When the reduction of the permanganate was complete, the ketone and unchanged hydrocarbon were extracted by ether directly from the mixture containing the oxides of manganese, the ether being distilled away and used over as far as possible to avoid loss by volatilization. From the oxidation of 30 grams of levo-laurolene a crude yield of 22 grams of the diketone was obtained. The crude product was taken up with a little ether, thoroughly dried with sodium sulphate and distilled in the vacuum obtained with a Sprengel pump, the distillate being condensed in a bulb surrounded with a mixture of ether and solid carbon dioxide.

The first fraction came over at ordinary temperature under 5 mm. pressure and consisted mainly of ether and the unchanged laurolene. A second fraction came over under 2mm. pressure at ordinary temperature and was laurolene. The third fraction, mainly laurolene, came over from 25-40° under 1/2 mm. pressure. The fourth fraction came over at the same pressure from 40-50° and was very small, consisting mainly of the diketone. The fifth and sixth fractions were taken under the same pressure at 50-67° and 70-80° respectively. The main bulk of the diketone came over fairly rapidly from 70-78° under a vacuum of less than I/2 mm. pressure.

Composition of Diketonefrom Levo-Laurolene.

The pure diketone,a heavy oil, gave on analysis:

Calculated for $C_8H_{14}O_2$;	C, 67.60	H, 9.86
Found ;	C, 66.98, 66.91, 67.47;	H, 9.90, 9.73, 10.23
Calculated for $C_8H_{15}O_2$;	C, 67.10	H,10.48
Calculated for $C_8H_{16}O_2$;	C, 66.65	H,11.10

The analysis of the diketone proved very difficult, for if burned in an open boat the results were uniformly too low for carbon; if burned in a small bulb partially filled with finely powdered copper oxide, it was extremely difficult to burn the last traces of carbon. In one experiment, when the Sprengel pump was working at its best the pure diketone was found to distil at 60°. The analysis of the oil is that given under (3) above and is in agreement with the theory within the limits of experimental error.

However the results prove beyond a doubt that the composition of the oxidation product of levo-laurolene is $C_8H_{14}O_2$, while the neutral nature of the oil, its reaction with phenyl hydrazine acetate solution and its failure to react with fuchsine aldehyde reagent show it to be a diketone.

The density determinations on the pure diketone gave $d\frac{15°}{15}=0.9881$ which shows that the diketone is an open chain compound.

Solid Diketone from Levo-Laurolene.

In the experiment where the diketone distilled at 60° under a Sprengel vacuum, a solid came over toward the end of the distillation. The yield was about 0.09 of a gram. The product melted at 68° (corr.) and gave upon analysis

Calculated for $C_8H_{14}O_2$	C, 67.60;	H, 9.86
Found	C, 67.00;	H, 10.50

Hence the solid is identical in composition with the liquid fractions and probably is the racemic form of the diketone.

Optical Activity of the Diketone.

The diketone, giving analysis (3) above, was found to be optically

active, $(\alpha)^{25^\circ}_{D} = -8.5^\circ$ in a 32.5% ether solution. In a more recent experiment, where the pure diketone came over in larger amounts at 70 - 78° under a pressure of about 1/2 m.m. the ketone was found to be very slightly optically positive $(\alpha)^{36.5^\circ}_{D} = 0.525^\circ$, while in a third experiment it was found to be inactive in a 25 alcoholic solution.

Hence it is evident that the diketone is a mixture of optical isomers as above prepared. It is very probable that at the temperature required for purification, the diketone may have suffered racemization, since heat may often cause the racemization of optically active compounds [1]. Further the racemization might easily occur during the oxidation. The resolution of the diketone into its optical isomers has not yet been attempted.

Phenyl Hydrazone of the Diketone from Levo - Laurolene.

All attempts to isolate a crystalline phenyl hydrazone of the diketone have failed. A liquid has always resulted which appeared to decompose, if dried for a few days in a vacuum desiccator.

The hydrazone was prepared by titrating the pure diketone with a freshly prepared N/10 Phenyl hydrazine acetate solution. The end point was determined by adding a drop of the hydrazine solution to a little Fehling solution. It was found that the phenyl hydrazine acetate solution decolorized the Fehling solution within 10 seconds while the hydrazone solution would not. In one determination using a charge of 0.1125 of a gram of the pure diketone 8.85 c.c. of the phenyl hydrazine acetate solution were required, while the theory for a diphenyl hydrazone would require 15.84 c.c. and that for a monophenyl hydrazone, 7.92 c.c. The oily hydrazone formed was extracted with ether and after drying the solution over fused sodium

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[1] See Julius B. Cohen -"Organic Chem. for Adv. Stu" Ed. 1907, p 80.

sulphate, the ether was distilled and the crude product analyzed.

Calculated for $C_8H_{14}(=N-NHC_6H_5)_2$; N, 17.40

Found N, 10.40

Calculated for $C_8H_{14}O(=N-NHC_6H_5)$; N, 12.59

A second preparation of the oily hydrazone was made by this method except that the theoretical amount of the phenyl hydrazine acetate solution for the diphenyl hydrazone was added, and the product formed extracted with ether. The dried hydrazone, freed from ether by suction with a water pump, gave on analysis:

(1) Calculated for $C_8H_{14}(=N-NHC_6H_5)_2$ N, 17.40

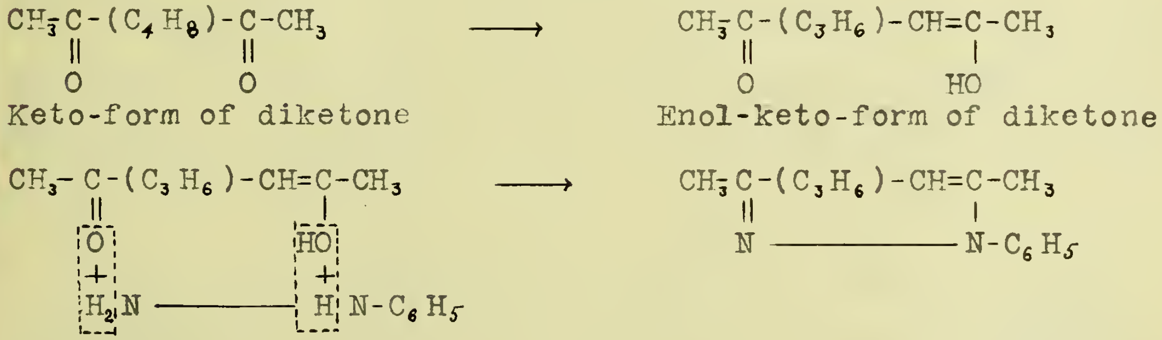
Found N, 12.72

(2) Calculated for $C_8H_{14}O\ (=N-NHC_6H_5)$ N, 12.07

(3) Calculated for $C_8H_{12}(=N-NHC_6H_5)$ N, 13.80

Hence one molecule of phenyl hydrazine has reacted with the diketone under these conditions. The explanation of the fact that a dihydrazone was not formed may be attributed to stearic hindrance.

Since the hydrazone could not be purified it is possible that the hydrazone may have the composition expressed by formula (3), which could be the hydrazone of the unsaturated monocyclic ketone which could be formed from the diketone by the elimination of water or which could be the condensation product represented by the following reaction:



$$CH_3-\underset{\underset{O}{\|}}{C}-(C_4H_8)-\underset{\underset{O}{\|}}{C}-CH_3 \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-(C_3H_6)-CH=\underset{\underset{HO}{|}}{C}-CH_3$$

Keto-form of diketone

Enol-keto-form of diketone

$$CH_3-\underset{\underset{\underset{\underset{H_2N}{+}}{O}}{\|}}{C}-(C_3H_6)-CH=\underset{\underset{\underset{\underset{H\,N-C_6H_5}{+}}{HO}}{|}}{C}-CH_3 \longrightarrow CH_3-\underset{\underset{N}{\|}}{C}-(C_3H_6)-CH=\underset{\underset{N-C_6H_5}{|}}{C}-CH_3$$

The former is unlikely as the attempts to form a condensation pro-

duct of the diketon will show. The latter is possible since where stearic hindrance may be present such reactions are rendered more probable. Yet the analysis appears to substantiate the view that a mono-phenyl-hydrazone of the diketone is formed at ordinary temperature.

Oxime of the Diketone.

Like the phenyl hydrazone, attempts to isolate a crystalline oxime have failed except in one case where a few crystals melting at 138.4° were obtained in too small amounts for analysis.

The oxime was prepared by dissolving 0.5 of a gram of the diketone in 5 c.c. of absolute alcohol to which 0.65 of a gram of hydroxylamine hydrochloride was added and then 1c.c. of a 33% sodium hydroxide solution. A little water was added to put all materials into solution. After two days no crystals had appeared so the solution was made just acid with acetic acid and extracted with ether. From the dried ether solution a nearly colorless viscous liquid was obtained which was dried in a desiccator over fused calcium chloride for two weeks, after which it was analyzed.

Calculated for $C_8H_{14}(=NOH)_2$ N, 16.27
Found N, 15.45
Calculated for $C_8H_{14}O(=NOH)$ N, 11.5

The analysis even though from a crude product is sufficiently accurate to prove that the oxidation product of laurolene is a diketone.

Condensation of the Diketone from Levo-Laurolene.

Experiment I. - Action of Dilute Sodium Hydroxide Solution.

One gram of the pure diketone was warmed with 50 c.c. of a 2% sodium hydroxide solution at the temperature of 60° while the flask and contents were continually shaken. The solution became dark red and by steam distillation about 0.1 of a gram of a product was obtained, which was carefully dried over anhydrous sodium sulphate and gave the analysis:

Calculated for	$C_8H_{12}O$	C, 77.41	H, 9.68
Found		C, 70.30	H, 10.41
Calculated for	$C_8H_{14}O_2$	C, 67.60	H, 9.86

Hence it is evident that no unsaturated monocyclic ketone was obtained by the condensation with sodium hydroxide and the process is extremely wasteful of the diketone, for the preparation of a few grams of which, months are required.

Experiment II. - Action of Heat on Diketone.

The pure diketone was placed in the boiling point apparatus as described by Mulliken in his book "The Identification of Pure Organic Compounds" and no evidence of the elimination of water was seen while very constant boiling points for the diketone were obtained.

Hence the diketone does not condense by heating to its boiling point under atmospheric pressure, much to the surprise of the writer.

Experiment III.

Very recently 1 gram of the diketone was treated with an excess of phosphorus pentoxide. Immediately upon the addition of the oxide the solution became a very dark green. After about two hours during which the solution and oxide were shaken carefully to mix thoroughly, an excess of water was added and a product distilled from the dark green mass, as a colorless oil. This was extracted from the water by ether and after careful drying, the ether was evaporated off by means of the water pump. The product was tested with a very dilute

potassium permanganate solution and gave evidences of unsaturation but since the diketone also reacts readily with permanganate no satisfactory conclusion as to its unsaturated nature could be drawn.

The boiling point of the product was determined in the apparatus described by Mulliken, mentioned above, and found to be 142 .8° under 750 m.m. pressure. The product blackened showing partial decomposition and rendered the determination very difficult. Here again the yield of the condensed product was very small showing that the condensation does not run smoothly and is very difficult to perform. Such small yields have been characteristic of the complete research and the time and patience required to prove a single point has made the investigation extremely difficult and tedious.

Semicarbazone of the Diketone from Levo-Laurolene.

3.3 grams of freshly prepared anhydrous potassium acetate were dissolved in a minimum amount of cold alcohol. 3.6 grams of the hydrochloride of semicarbazide were dissolved in a minimum amount of cold water and this solution added to the former. This mixture was then added to 1.8 grams of the crude diketone obtained by oxidizing 5 grams of levo-laurolene. The whole was filtered to remove dust and dirt and stoppered for a few hours, then allowed to evaporate in the air. Since after two days no crystalls had separated the solution was removed to a vacuum desiccator. After four days 0.35 grams of crystals were recovered and after washing with alcohol were desiccated over fused calcium chloride and potassium hydroxide. A week later a second crop of 0.20 of a gram was recovered and treated like the first crop. The melting point of this product was 193.6° (corr.) and gave on analysis:

Calculated for $C_8H_{14}(=N-NHCONH_2)_2$ N, 32.81

Found N, 28.98, 29.50

A residue was noted in the combustion boat which gave a test for chlorides. The original crystals also gave a test for chlorides. Hence the product was contaminated with potassium chloride. Accordingly, the crystals were finely powdered and extracted with 25 c.c. of warm water and carefully washed free from chloride after filtering. The crystals melted at 195.2°(corr.) after drying in vacuo over calcium chloride and the analysis gave:

Calculated for $C_8H_{14}(=N-NHCONH_2)_2$ N, 32.81; C, 46.87; H, 7.82

Found N, 31.71; C, 46.50; H, 8.80

But since the semicarbazone was so insoluble in all solvents tried it could not be purified. Moreover, the great difficulty in getting enough material to work with caused the analyses to be made on charges usually less than 0.035 of a gram, which are decidedly too small for satisfactory work with the ordinary analytical methods.

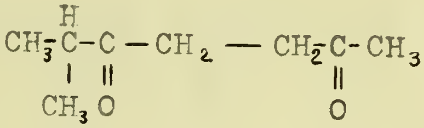
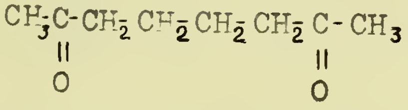
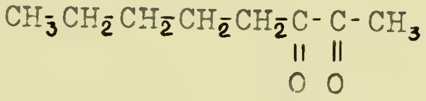
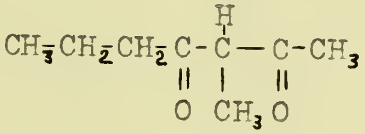
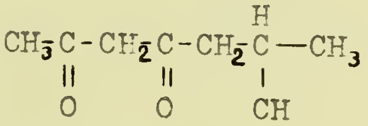
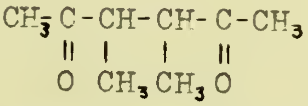
It appears, however, that a disemicarbazone is formed which is not the disemicarbazone of diacetyl butane which Perkins found to melt at 220° .

Boiling Point Determination of Diketone.

Using the method described by Mulliken, a preliminary test of the boiling point gave about 200° . A new sample of the diketone was then taken and when the sulphuric acid bath was at a temperature of 220°, the tube containing the diketone was lowered into the acid which was thoroughly stirred. Equlibrium between external atmospheric and internal vapor pressures occurred at 203.6°(corr.) at 750 m.m. pressure as determined by different experiments over a

range of several days. A slight yellowing of the liquid was observed, but no other decomposition was noted.

The boiling point shows the oxidation product of levo laurolene to be an open chain diketone for comparison with its isomers gives the following substantiation:

Name.	Structure	Boiling point	Sp. Gr.
Diketon from l-laurolene.		750 m.m. 203.6°	$d_{20}^{20}=0.9881$
γ,ζ Diketo β Methyl heptane	 $CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{O}{\underset{\Vert}{C}}-CH_2-CH_2-\underset{O}{\underset{\Vert}{C}}-CH_3$	23 m.m. 102 - 106°	$d^{20°}=0.9402$
β,η Diketo octane	 $CH_3-\underset{O}{\underset{\Vert}{C}}-CH_2-CH_2-CH_2-CH_2-\underset{O}{\underset{\Vert}{C}}-CH_3$	m.p. 43 - 44°	
β,γ Diketo octane	 $CH_3CH_2CH_2CH_2CH_2\underset{O}{\underset{\Vert}{C}}-\underset{O}{\underset{\Vert}{C}}-CH_3$	732.8 m.m. 172-173°	$d_4^{19}=0.8814$
β,δ Diketo-γ- Methyl heptane	 $CH_3CH_2CH_2\underset{O}{\underset{\Vert}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{O}{\underset{\Vert}{C}}-CH_3$	20 m.m. 89 - 90°	$d_4^{0°}=0.955$
δ,ζ Diketo-β-Methyl heptane	 $CH_3\underset{O}{\underset{\Vert}{C}}-CH_2\underset{O}{\underset{\Vert}{C}}-CH_2\underset{CH}{\overset{H}{C}}-CH_3$	19 m.m. 76°	$d_4^{0°}=0.936$
β,ε Diketo-γ-Dimethyl Hexan	 $CH_3\underset{O}{\underset{\Vert}{C}}-\underset{CH_3}{CH}-\underset{CH_3}{CH}-\underset{O}{\underset{\Vert}{C}}-CH_3$	210°	

From this table it is evident that the oxidation product of levo-laurolene is an open chain diketone. Its boiling point 203.6° at 750 m.m. pressure as well as its density shows that the keto groups must be removed from each other by more than two carbon atoms since the nearer together the carbonyl groups the lower the boiling point and density as the table shows.

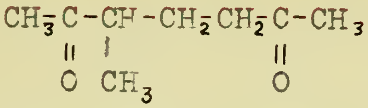
Oxidation of the Diketone.

The diketone from levo-laurolene was treated with the required

amount of sodium hypobromite for two acetyl groups by adding slowly and allowing the product to stand two hours surrounded by an ice water bath. The hypobromite was prepared by aspirating bromine into twice the required amount of a 10% sodium hydroxide solution which was cooled by an ice bath to prevent the formation of any bromate. Just the required amount of hypobromite for two acetyl groups was used up and bromoform separated, which was a solid at the temperature of the ice bath. It was extracted by ether and after the ether was removed fron the residue, it was acidified with a slight excess of a 10 per cent. sulphuric acid solution and again extracted with ether. The evaporation of the dried ether solution left a viscous oil which partially crystallized but all attempts to isolate crystals in sufficient quantity to determine their melting point have thus far failed. The oil was acid and the behavior of its salts was in agreement with those of α methyl glutaric acid. Lack of time has prevented establishing the absolute identity of this product, but it again substantiates the view that the oxidation product of levo-laurolene is a diketone.

Properties and Structure of the Diketone from Levo-Laurolene.

The diketone possesses the boiling point of 203.6° under 750 m.m. pressure without undergoing decomposition or condensation. Under certain conditions it may be obtained as a solid melting at 68° (cor.). It appears to be optically active $(\alpha)_D^{25^\circ} = -8.5^\circ$ and $(\alpha)_D^{36.5^\circ} = 0.525^\circ$ and therefore a varying mixture of optical isomers. It yields a liquid monophenyl hydrazone, a liquid dioxime and a disemicarbazone melting at 193.6° corrected. Upon oxidation it appears to yield α methyl glutaric acid and has therefore the formula:



$$CH_3-\underset{\overset{\|}{O}}{C}-\underset{\overset{|}{CH_3}}{CH}-CH_2-CH_2-\underset{\overset{\|}{O}}{C}-CH_3$$

which will receive more support from what follows.

DEXTRO LAUROLENE.

Preparation of Dextro Laurolene.

The method of preparation of dextro laurolene is essentially the same as that given by Noyes.[1] 41.5 grams of the hydrochloride of aminolauronic acid, which had been carefully purified by extraction with ether and subsequent crystallization were dissolved in a minimum amount of water by gently warming. After thoroughly cooling, 13.4 grams of sodium nitrite, dissolved in 35 c.c. of water were carefully added to the aminolauronic acid solution by introduction to the bottom of the flask by means of a pipette so as to form a distinct layer. Thus the nitrite solution slowly diffused into the acid solution and the decomposition proceeded so slowly (under a reflux condenser) that no evidence of escaping nitrous acid fumes is seen, providing the flask is cooled with ice water for the first hour. At the end of three hours, 2.5c.c. of a 40 per cent. hydrochloric acid solution were added and the solution allowed to stand for another hour. After the first two hours, the flask and contents were shaken occasionally to insure complete mixing of the two solutions. At the end of four hours the decomposition was considered complete and 40 c.c. of a 10 per cent. sodium carbonate solution were added and the whole heated to boiling and the hydrocarbon distilled with the first 20 c.c. of water. This distillate was shaken with 2 c.c. of a 10 per cent. sodium hydroxide solution and the hydrocarbon after separation and drying over anhydrous sodium sulphate was distilled. The main product distilled between 120.3 and 122°. The steam distilled product after drying, gave a yield of 4.5 grams or 10.9 per cent. of the hydrochloride taken.

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[1] W.A.Noyes. Am. Chem. J. 17 (1895)-432.

Physical Constants of Dextro - Laurolene.

Noyes [1] had found the hydrocarbon prepared by the above method to possess the composition C_8H_{14} and to contain one double union. His density determinations gave $d^{15}_{15}=0.8033$, and $d^{20}_{20}=0.8004$, while the boiling point of the hydrocarbon he stated to be 122.°

In the present work, the density determinations gave $d^{15}_{4}=0.8030$ and $d^{20}_{4}=0.7991$. The boiling point was 120.3 - 121° under 750 m.m. pressure. The hydrocarbon prepared by this method was always optically positive. A determination of its optical activity made five hours after the above described decomposition of the aminolauronic acid was complete gave $(\alpha)^{23}_{D}=22.83°$; while the optical activity of an old preparation freshly distilled gave $(\alpha)^{15}_{D}=23.62°$. One preparation made in the month of August and allowed to stand about two months gave $(\alpha)^{26.2}_{D}=28.15°$ but less care was used to duplicate exactly the above proceedure and this may have been responsible for the change in its activity. It is evident, however, that a given product does not suffer mutarotation upon standing and further that dextrolaurolene, like levo laurolene, is a mixture of optical or possibly structural isomers.

Hence levo-laurolene and dextro-laurolene possess the same composition, boiling point and density but differ apparently only in their optical properties. In the levo form the levo isomer is in excess while in the dextro form the dextro isomer is in excess. Further different methods of preparation give a different proportion of the two isomers and hence each has a varying value for its optical activity.

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[1] W.A.Noyes. Am. Chem. J. 17, 432 (1895).

Diketone of Dextro-Laurolene.

Oxidations of dextro-laurolene were carried out by the same methods as those given under levo-laurolene and with the same results. The diketone of dextro-laurolene was prepared by the method given under the preparation of the diketone of levo-laurolene. The product was purified by fractional distillation in a Sprengel vacuum, the receiver being cooled with solid carbon dioxide and ether. The first fraction came over at ordinary temperature under 1 m.m. pressure and consisted of the unchanged hydrocarbon. The second fraction was taken from 30 - 40° under about 1/2 m.m. pressure and was largely the unchanged hydrocarbon. The third fraction was taken fron 40 -50°, the fourth fraction from 50 - 60°, the fifth fraction from 60 - 70°, and the final fraction fron 70 - 90°, all of which consisted of the pure diketone. The bulk of the product was contained in the fourth and fifth fractions the latter gave on analysis:

Calculated for $C_8H_{14}O_2$	C, 67.60	H, 9.86
Found	C, 66.53, 66.5, 67.9(3);	H, 9.90, 10.15, 10.60(3)
Calculated for $C_8H_{15}O_2$	C, 67.10	H, 10.48
Calculated for $C_8H_{16}O_2$	C, 66.65	H, 11.10

As stated under the diketone of levo laurolene it was exceedingly hard to burn the last traces of carbon, but extra long burning at a high temperature gave analysis (3) which is within the range of experimental error.

The analyses agree best for $C_8H_{14}O_2$ and therefore the oxidation product of dextro laurolene is also a diketone, whose physical constants show it to be identical with the diketone obtained from levo-laurolene, supporting the view that the two hydrocarbons are different mixtures of optical isomers.

Optical Activity of the Diketone.

Several determinations of the optical activity of the diketone oxidation product from dextro-laurolene showed it to be optically inactive. Experiments were performed with diketone in the pure form as well as in 20.5 per cent. ethereal solution.

Oxime and Hydrazone of the Diketone.

The same results as those given under the diketone from levo-laurolene were obtained with the diketone fron dextro laurolene, namely oils in each case.

Semicarbazone of the Diketone.

The semicarbazone was prepared in the same manner as given under the diketone from levo-laurolene. A product melting fairly sharply at 190° was obtained after the mother liquor had stood several months, which gave upon analysis:

Calculated for $C_8H_{14}(=N-NHCONH_2)_2$; N, 32.81

Found N, 33.25

This product, melting originally at 190°, was remelted. It melted at 192°(cor.) then resolidified and finally melted to a greenish red oil at 224 - 225°. Recently the preparation of the semicarbazone has been repeated. After the mother liquor had stood some time a gummy organic mass remained, which was removed and after extracting with ether, was triturated with alcohol and a floculent organic precipitate was formed which was poured off fron the remaining gummy material and after washing and drying gave a sharp melting point at 227.9°(cor.). No evidence of a preliminary melting at 192° was noted. Lack of time has prevented an analysis of this product but its melting point

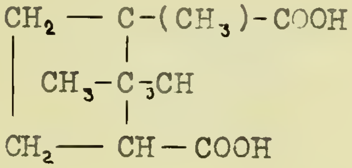
agrees with the higher melting product obtained from the preparation giving the above analysis. From this rather unsatisfactory work, the balance of the evidence appears to be in favor of the fact that a disemicarbazone is formed showing the oxidation product of dextro-laurolene is also a diketone.

Structure of the Diketone from the Oxidation of Dextro-Laurolene.

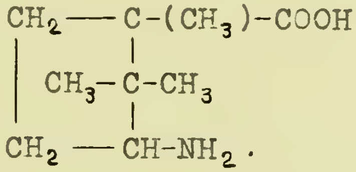
The boiling point and general behavior of the diketone from dextro-laurolene makes it evident that it is identical with the diketone obtained from levo-laurolene. Further work upon this product will be necessary for its complete identity.

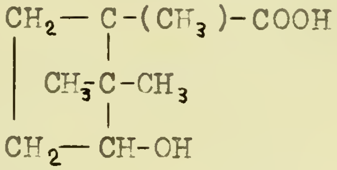
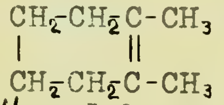
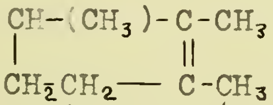
STRUCTURE OF LAUROLENE.

From the above work it is evident that dextro- and levo-laurolene are different mixtures of optical isomers of the same configuration. Komppa's [1] synthesis of camphoric acid has definitely proved its structure to be



W.A.Noyes' work, as well as that of other investigators, has proven definitely that if the above is the structure of camphoric acid, then amino lauronic acid must have the structure



Giving amino lauronic acid the above structure, then the action of nitrous acid upon it should produce  , but hydroxylauronic acid being unstable loses water and carbon dioxide simultaneously yielding dextro laurolene. From the fact that a diketone oxidation product is obtained from laurolene and that amino-lauronic acid has the above structure only two configurations are possible for laurolene:  and 

1,2 Dimethyl Δ' cyclohexene 1,2,3 Trimethyl Δ' cyclopentene.

The physical properties of dextro-laurolene show that it cannot be a cyclo-hexene derivative as the work given in the historical introduction and the experimental part prove.

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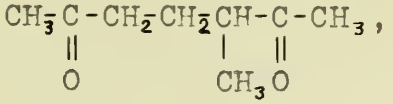
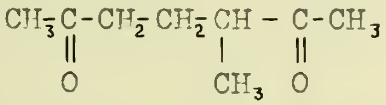
[1] Komppa 34, 2472 (1901), 36, 4332 (1903).

1,2 Dimethyl Δ' cyclohexene would yield diacetyl butane, $(CH_3-CO-CH_2-CH_2-C_2H_4-COCH_3)$ upon oxidation; while 1,2,3, trimethyl Δ' cyclopentene would give,  $CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-CH_3$, 3 methyl, 2,6 heptadione.

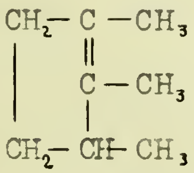
Perkin [1] has prepared diacetyl butane and found it to be a solid melting at 43-44°, which could not be distilled without condensation and which gave an oily oxime and hydrazone.

The above experimental work shows that dextro-laurolene yields a liquid diketone which may be distilled in vacuum without condensation or decomposition. The boiling point determinations of the diketone from levo-laurolene show that it will not condense at its boiling point under atmospheric pressure. Hence it is not identical with diacetyl butane and must have the structure



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-CH_3$$

and therefore laurolene has the structure of 1,2,3,trimethyl cyclopentene,



Laurolene could not be 1,2 dimethyl Δ' cyclohexene since such a structure contains no assymmetric carbon atom while laurolene is always optically active. Hence the proof that laurolene upon oxidation will yield an open chain diketone of the composition $C_8H_{14}O_2$ proves definitely that its structure is 1,2,3,trimethyl Δ' cyclo-pentene, since the structure of aminolauronic acid admits of no other possibility fulfilling the properties that laurolene possesses.

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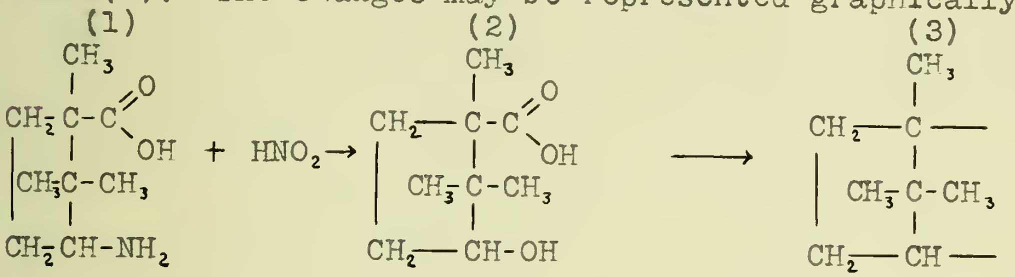
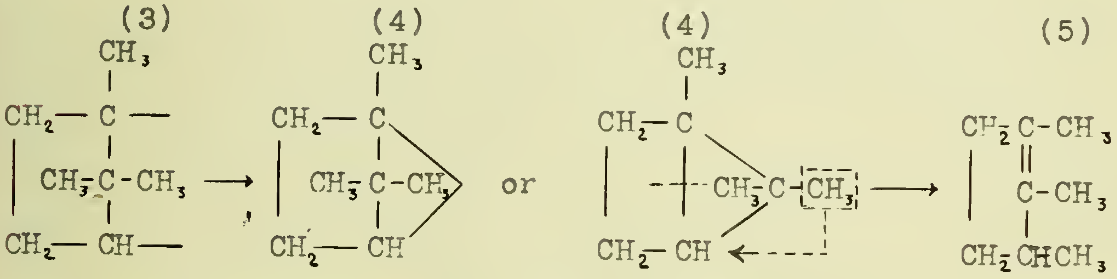
[1] Perkin - Soc. 57, 241.

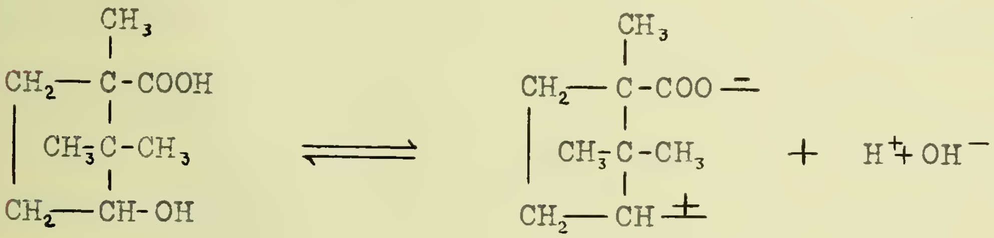
Mechanism of the Reaction by which Laurolene is Formed.

The reaction of nitrous acid upon amino lauronic acid (1) should produce hydroxylauronic acid (2). This acid being unstable loses carbon dioxide and water forming the free radical (3) below. But since a free radical cannot exist, the two free bonds neutrallize each other producing the unstable bicyclic compound (4), which suffers rearrangement into the more stable 1,2,3,trimethyl Δ^{1}cyclopentene (5). The changes may be represented graphically as follows:





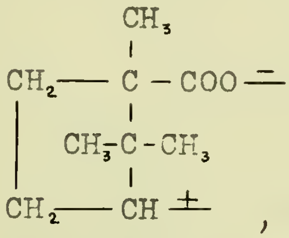
Since hydroxylauronic acid is an amphoteric electrolyte the following ionization is possible:

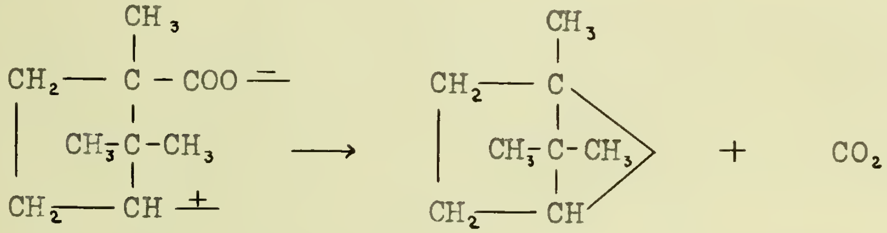


The hydrogen and hydroxyl ions would unite to form water until the concentration of these ions was reduced to that of water under the given condition. Now the formation of the bicyclic compound may be considered as due to the neutralization of these two opposite charges thus:

But in the electrolysis of organic acids, the acid ion travelling to the anode is neutrallized and carbon dioxide is always liberated causing two radicals to unite as follows

$2\ (R\text{-}COO^{-}) + 2\ (+) \longrightarrow R{-}R + 2\ CO_2$

Similarly, in the neutrallization of the negative charge on the "zwitter ion",  , by its own positive charge carbon dioxide would be eliminated and the bicyclic compound (3), mentioned above, would result:



Whether or not this bicyclic compound would rearrange depends upon the relative stability of the different isocyclic rings. Baeyer's strain theory states that the trimethylene ring is very unstable and would under these conditions easily rearrange to produce the stable cyclo-pentene ring, as follows:

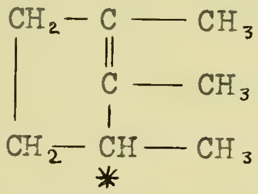
The oxidation to a diketone shows that this rearrangement has

occurred and that 1,2,3 trimethyl Δ'cyclopentene resulted.

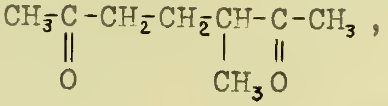
Conclusions.

I. The so called dextro- and levo-laurolenes are different mixtures of the true d-and l-laurolenes. The proportion in which these two optical isomers occur in any preparation varies with the method.

II. The configuration of laurolene is 1,2,3 trimethyl Δ'cyclopentene;



III. The diketone oxidation product of laurolene possesses the structure



$$CH_3-\underset{\underset{O}{\|}}{C}-CH_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{O}{\|}}{C}-CH_3$$

, 3 methyl 2,6 heptadion.

In conclusion the writer wishes to thank the members of the graduate faculty of the University of Illinois who have been associated with him in this work, and especially Dr. W. A. Noyes, under whose direction this work has been carried out.

BIOGRAPHICAL.

The writer received the degree of Bachelor of Science from Worcester Polytechnic Institute in the year 1906, graduating with first honors, and the degree of Master of Science from the University of Illinois in the year 1909. The summer of 1906 was spent in research at Worcester Polytechnic Institute upon the imide color bases of the tryphenyl methane dyestuffs under the direction of Dr. W. L. Jennings. The academic year 1906 - '07 was spent as research assistant to Dr. F. J. Moore at the Massachusetts Institute of Technology. The investigation was upon the imide base made from benzophenon together with attempts to isolate diphenylbromaminomethane. The seminaries of the physical chemistry department were also attended. The writer taught organic chemistry at the same institution during the 1907 summer school. The academic year 1907-'08 was spent at the University of Illinois as lecturer and research assistant to Dr. W.A. Noyes. The academic years 1908 to 1910 were spent at the same institution as assistant in organic chemistry. The summers of 1908 and 1909 were spent respectively as assistant in general chemistry and in charge of the organic chemistry in the summer school of the University of Illinois.

During the year 1907, the writer developed a method for the water-proofing of cement concrete which is controlled by the Eastern Expanded Metal Co. of Boston, Massachusetts. Other investigations upon cement concrete and allied construction materials were carried out.

The writer is a member of the American Chemical Society, the Illinois Academy of Science, Sigma Xi, and Phi Lambda Upsilon.

The writer's publications are as follows:-

(1) Molecular Rearrangements in the Camphor Series.
II. Laurolene. W. A. Noyes and C. G. Derick.
Journal of the American Chemical Society, Vol. XXXI, (1909) - 669.

(2) Methods of Waterproofing Concrete. C. G. Derick.
Illinois Technograph, 1909.
Engineering and Contracting Journal. Vol. XXXII. (1909) - p. 175.
Scientific American Supplement No. 1773 Vol. LXVIII. Dec. 25, 1909. p. 406.

(3) Notez zur Darstellung von Benzophenonimid Derivaten. With F.J. Moore. Berichte Vol. XXXXIII. p. 563.